ENGINEERING ASPECTS OF CALCIUM CARBONATE AND MAGNESIUM HYDROXIDE PRECIPITATION IN WASTE WATER RECLAMATION

by

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DECLARATION OF CANDIDATE

I, Hermannus Nikolaas Sybrandus Wiechers, declare that this thesis is my own work and that it has not been submitted for a degree at another university.

Signed by candidate

APRIL, 1978

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THESIS CONTRIBUTION TO KNOWLEDGE

This thesis attempts to resolve some of the major problems associated with lime treatment in waste water reclamation. The contribution to knowledge is briefly outlined below.

Lime-treated effluent instability

One of the major problems associated with lime treatment is the instability of lime-treated effluent, which may result in serious calcium carbonate scale formation problems. In the thesis this instability is attributed to two fundamental causes,

(1) Incomplete precipitation, i.e. a kinetic problem.

(2) The unintentional absorption of carbon dioxide from the air by the highly alkaline lime-treated effluent, i.e. a contamination problem.

Calcium carbonate and magnesium hydroxide precipitation are time dependent. As a consequence of this time dependency unstable effluent may be produced under reaction conditions commonly encountered in practice. An exhaustive study identified the major factors affecting the precipitation kinetics. Reaction system conditions required for producing a stable effluent are,

(1) Lime slurry and sludge, in that sequence, must be thoroughly mixed with the waste water, preferably by means of in-line static mixers, before discharge to a completely stirred tank reactor.

(2) A completely stirred tank reactor with a minimum mean residence time of two minutes must be provided for the dissolution and precipitation reactions to go as near to completion as possible.

(3) The reactor contents must have a sludge concentration of the order of 10 000 mg ℓ^{-1}.

With these conditions provided for the kinetic considerations become of minor importance, i.e. equilibrium or near equilibrium will be attained.

Observations on the Stander Water Reclamation Plant indicated that scale formation in pipes and pumps positioned downstream of the lime treatment process is due to the absorption of small quantities of carbon dioxide by the highly alkaline lime-treated effluent at clarifier weirs, troughs and sumps. It was concluded that the scaling problem will be solved satisfactorily only if carbon dioxide absorption is eliminated or minimized. Carbon dioxide absorption can possibly be limited by modifications to the design of the clarifier and ancillary units, for example by covering weirs, troughs and sumps to minimize the free movement of air over the alkaline lime-treated effluent.

Predictive model

In design of lime treatment plants one of the main problems is the adequate prediction of the effluent lime demand, treated effluent quality and sludge generation rate. In the thesis it is shown that good predictions can be obtained by applying the equilibrium model of Loewenthal and Marais for the carbonic-calcium-magnesium-water system, by replacing the thermodynamic solubility products for calcite and brucite in their model by "apparent" solubility products - pK_{CaCO_3} = 6,7 and $pK_{Mg(OH)_2}$ = 10,5, respectively. Successful prediction of the quality of lime-treated secondary effluent for waste waters from different origins with significantly different constitutions, demonstrated the model's potential as a generalized predictive technique. The same technique was applied to determine the quality of recarbonated effluent, the suitable model pK_{CaCO_3} value in this case being 7,1.

Design guidelines

From the findings on the kinetics of precipitation and equilibrium behaviour of the lime-waste water system, process design guidelines for the lime treatment process as applied in water reclamation are presented, providing simple practical solutions.

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RESUME

High lime treatment is commonly used as the first unit process in a train of unit processes utilized for reclaiming waste water, the reason being that this process efficiently removes phosphates, organic matter, magnesium hardness, carbonate hardness and heavy metals; prepares the water for ammonia stripping and results in waste water disinfection and clarification. A major drawback associated with the process is the instability of the effluent after lime treatment, which results in post-precipitation of calcium carbonate in subsequent unit processes. Often this post-precipitation is in the form of hard scale which results in serious practical problems such as : flow reductions, blockages in pipes, seizure of pumps, water flow maldistribution in ammonia stripping towers and mudball formation in sand filters.

The investigation into calcium carbonate and magnesium hydroxide precipitation reported in this thesis was undertaken in order to come to a better understanding of the factors which govern these reactions. It was anticipated that the knowledge gained in this study could be used for optimizing the design of precipitation processes for water reclamation plants.

Initially it was thought that the severe scaling problems associated with the high lime treatment on the Stander Water Reclamation Plant (Pretoria, South Africa) were a result of insufficient reaction time being allowed for the lime-secondary effluent reactions, since the residual calcium concentration in treated effluent was significantly higher than that predicted from the calcium carbonate (calcite) solubility product. For this reason the major effort at the beginning of this investigation was directed at kinetic studies of $CaCO_3$ precipitation.

Pure synthetic system $CaCO_3$ precipitation kinetics

Precipitation kinetics studies were commenced by studying pure synthetic calcium carbonate solutions. This choice of reaction system was made in order to determine the effects of the basic system parameters such as : the dissolved calcium and carbonate ion and seed $CaCO_3$ concentrations, as well as temperature, pH and turbulence in the reactor solution on the kinetics of $CaCO_3$ precipitation without the additional effects of phosphates, magnesium and organic matter which are also present in secondary effluent. The precipitation experiments were conducted under conditions simulating calcium and alkalinity concentrations, and pH and temperature normally encountered in lime and recarbonation processes in water reclamation plants.

Preliminary tests indicated that pure system $CaCO_3$ precipitation under these simulated plant conditions may be very rapid. Experimental techniques reported in the literature for monitoring $CaCO_3$ precipitation, e.g. measurement of residual calcium and pH with time, are inadequate for studying rapid $CaCO_3$ precipitation, due to the uncertainty associated with the accurate determination of rapidly changing residual calcium. This problem was overcome by developing a calculational procedure based on the equilibrium chemistry of the ionic species of the calcium-carbonic-water system. With this procedure it is necessary to monitor pH with time to obtain a complete description of the time behaviour of $CaCO_3$ precipitation. The only limitations in this technique are the pH probe response time (which is of the order of one second) and an upper limiting pH, approximately pH 10,5. The latter limitation is due to two effects : the method becomes approximate due to the omission of the $CaOH^+$ ion pair in the calculational procedure and insensitive due to the relatively high mass of $CaCO_3$ that is precipitated for only a slight change in pH. Both homogeneous and heterogeneous $CaCO_3$ precipitation from pure synthetic calcium carbonate solutions were studied using this monitoring technique. Four conclusions were drawn from the results obtained from homogeneous $CaCO_3$ precipitation experiments.

(1) The $CaCO_3^o$ ion pair in the pH range 9,5 and higher, significantly affects the dissolved species concentration distribution. In solutions with typical waste water calcium and alkalinity concentrations at a pH of 10,0, up to 30 percent of the solution total dissolved calcium is in the $CaCO_3^o$ form. For this reason ion pairing considerations were included in all subsequent calculation procedures for the calcium-carbonic-water system.

(2) Ion pairing reactions are extremely rapid. Within one second of mixing solutions of calcium with carbonate in batch experiments, the pH of the reaction mixture fell by approximately 0,2 of a pH unit and then stabilized at a fixed value. Experimental verification that ion pairing reactions are very rapid, justified the use of the pH only monitoring technique and its associated calculational procedure, since a basic assumption inherent in this procedure is that the ionic reactions are near instantaneous or at least one to two orders of magnitude more rapid than the $CaCO_3$ precipitation reaction.

(3) Experimentally determined induction periods associated with homogeneous $CaCO_3$ precipitation in batch and plug-flow reaction systems, of 1 to 5 minutes or longer, indicate that plug-flow reactors without sludge recycling should not be used in recarbonation - softening processes. However, even without sludge recycling completely stirred tank reactors (CSTR's) should develop sufficient seed virtually to eliminate the induction period.

(4) Homogeneous $CaCO_3$ precipitation in CSTR systems gives rise to severe scale formation on all surfaces in contact with the reacting solution. The formation of scale (epitaxial growth) appeared to be characteristic of solutions reacting without inoculated $CaCO_3$ seed. These results were confirmed by experience with homogeneous $CaCO_3$ precipitation in the full-scale plant, where severe scale formation took place on the surfaces of the recarbonation-softening reactor and associated pipes transporting effluent.

It was not attempted to formulate a model for homogeneous $CaCO_3$ precipitation kinetics, because of the inherent lack of knowledge of any quantitative estimate of the surfaces available for growth in such systems. Preferential precipitation on the reactor surfaces rather than on the $CaCO_3$ crystals generated in the reaction solution makes even estimates of surface available for crystal growth impossible. Another consideration is the generation of self-seeding precipitates in CSTR reactor systems which results in a change of precipitation type, i.e. from homogeneous to heterogeneous precipitation soon after commencing a continuous homogeneous precipitation run.

In heterogeneous $CaCO_3$ precipitation experiments high seed masses were inoculated into the reaction solutions, supplying sufficient crystal growth sites in the solutions almost completely to suppress epitaxial $CaCO_3$ growth on reactor surfaces. Heterogeneous $CaCO_3$ precipitation was studied in batch reactor systems for a wide range of calcium, alkalinity and $CaCO_3$ seed crystal concentrations, as well as pH, temperature and reactor stirring speed. In any particular experiment, the crystallization process appears to conform to the model for calcium removal proposed by Reddy and Nancollas (1971),

$$\frac{d[Ca_T^{2+}]}{dt} = k_G . CaCO_3(s) . \{ [Ca^{2+}] [CO_3^{2-}] - \frac{K_{sp}}{f_D^2} \} \quad .... \quad (R.1)$$

where $d[Ca_T^{2+}]/dt$ = rate of change in total dissolved calcium with time (mol ℓ^{-1} min^{-1})

k_G = rate constant for crystal growth (ℓ mol^{-1} min^{-1})/(mg seed ℓ^{-1})

$CaCO_3(s)$ = concentration of $CaCO_3$ suspended in solution (mg seed ℓ^{-1})

[ ] = enclosed species concentration (mol ℓ^{-1})

K_{sp} = calcite solubility product (mol^2 ℓ^{-2})

f_D = activity factor for divalent ions

{ } = degree of supersaturation (mol^2 ℓ^{-2})

The rate constant for $CaCO_3$ crystal growth, k_G, is temperature dependent according to the Arrhenius relationship,

$$k_G = A.\ e^{-E/RT} \qquad \ldots\ (R.2)$$

where A = constant
E = activation energy (kcal mol^{-1})
R = gas constant (kcal $mol^{-1}\ {}^{o}K^{-1}$)
T = absolute temperature (degree Kelvin)

with the activation energy, E = 10,3±0,9 kcal mol^{-1}. The k_G value is independent of stirring speed and crystal seed concentration (for crystal seed concentrations greater than a critical minimum value of 400 mg ℓ^{-1}), but apparently dependent on the initial ionic equilibrium pH value, pH_o. This inconsistancy was resolved when modelling the data according to the rate equation proposed by Sturrock, Benjamin, Loewenthal and Marais (1976),

$$\frac{\delta[CaCO_3]}{\delta t} = k_G.CaCO_3(s).f_D^2\{[Ca^{2+}]^{\frac{1}{2}}\ [CO_3^{2-}]^{\frac{1}{2}} - (\frac{K_{sp}}{f_D^2})^{\frac{1}{2}}\} \qquad \ldots\ (R.3)$$

Rate Equation (R.3) holds for both batch and continuously stirred tank reactor systems.

The second order dependence of the rate of $CaCO_3$ precipitation on the supersaturation term (see Eq. R.3), the relatively high activation energy and the independence of k_G on stirring speed, are all consistant with a surface controlled growth mechanism for $CaCO_3$ precipitation under the specific conditions choosen in these experiments, i.e. simulated lime treatment and recarbonation softening process conditions.

A number of heterogeneous $CaCO_3$ precipitation experiments were conducted with calcium carbonate crystals from different chemical suppliers. The rate constant for $CaCO_3$ crystal growth for these crystals

from different origins differed by as much as a factor of five. This discrepancy in k_G values arises as a result of the inability to quantify the "active" surface available for $CaCO_3$ crystal growth.

The inability to quantify "active" surface available for crystal growth and also the suspected many complex effects reigning in lime-waste water systems, lead to a reappraisal of the significance of pure synthetic system studies in characterizing $CaCO_3$ and $Mg(OH)_2$ precipitation in lime-waste water systems. After a study of the situation and in particular taking into consideration the urgency to find practical solution procedures (as voiced by the engineers), it was decided to redirect the investigation from a fundamental to a more practical approach and an investigation of $CaCO_3$ and $Mg(OH)_2$ precipitation in lime-treated secondary effluent was undertaken.

Four aspects relating to the lime-secondary effluent reactions were studied,

(1) lime dissolution kinetics,
(2) reactions in batch reaction systems,
(3) reactions in continuously stirred tank reactor systems, and
(4) characterization of final or "equilibrium" states.

Lime dissolution kinetics

The simplistic rate equation for lime dissolution proposed by Jenkins and Lee (1976),

$$-\log(1-[OH^-]/[OH^-]_\infty) = k.t \qquad \ldots. \quad (R.4)$$

where $[OH^-]$ = hydroxide ion concentration (mol ℓ^{-1}) at time = t
$[OH^-]_\infty$ = hydroxide ion concentration (mol ℓ^{-1}) at time = ∞
k = proportionality constant (min^{-1})
t = time (min)

was shown to model lime dissolution adequately in secondary effluent in batch reactor systems, when k = 0,21 min^{-1}. It is clear from predictions made using Eq. (R.4) that lime dissolution in secondary effluent is time dependent and requires of the order of 5 or more minutes for approximately complete lime dissolution. Practical solutions to overcome this problem have been proposed by Mennell, Merill and Jorden (1974) and Jenkins and Lee (1976). Mennell *et al* suggested the use of "split" lime treatment, i.e. predissolving the lime in a "split" stream (± 15 percent) of the mainstream, before adding the "split" to the mainstream. Jenkins and Lee suggested predissolving lime in a recycled stream (± 15 percent of base flow) from the clarifier overflow, the advantage being that lime dissolution is apparently less inhibited in treated effluent than in raw effluent. In the investigation reported in this thesis approximately complete lime dissolution was attained by utilizing intense mixing of lime with secondary effluent by means of an in-line static mixer followed by a short retention time CSTR (± 2 minutes). The static mixer is placed in the influent pipe just upstream to the discharge point for influent into the CSTR system.

Lime-waste water reactions in batch reactor systems

A study of lime-secondary effluent reactions in the pH range 10,0 to 11,6, in the absence of inoculated sludge in batch reactor systems, indicated that $CaCO_3$ and $Mg(OH)_2$ precipitation takes place in two phases, an initial rapid phase followed by a slow secondary phase. The initial rapid precipitation is complete within 2 to 3 minutes after adding lime to the secondary effluent. Slow secondary precipitation takes place over far longer reaction periods, i.e. even at reaction periods of 90 minutes residual calcium and magnesium concentrations were not completely stabilized.

Lime-waste water reactions in CSTR systems

Studies on continuously stirred tank reactor (CSTR) systems yielded similar results to those from the batch reaction systems, i.e. two phases of precipitation, initial rapid precipitation at short CSTR residence times and slow secondary precipitation at longer residence times. Investigation into various alternative reaction system configurations for continuous lime treatment suggested a configuration which minimizes the problems of slow lime dissolution and slow secondary precipitation of $CaCO_3$ and $Mg(OH)_2$. Lime and recycled sludge from the settling systems underflow were added to the secondary effluent prior to the solution discharge into a CSTR reactor. Both lime and sludge are intensely mixed with the secondary effluent by means of in-line static mixers, the lime being added at a point in the influent line upstream to the point of sludge addition. With reaction solution sludge concentrations of the order of 10 000 mg ℓ^{-1}, stable CSTR effluents were obtained in relatively short CSTR residence times of 1 to 2 minutes. Furthermore, the sludge recirculation significantly reduced the residual calcium and magnesium concentrations in reactor effluent. With these short reaction times the need for formulating the kinetics of $CaCO_3$ and $Mg(OH)_2$ precipitation for lime-secondary effluent reactions fell away, since procedures to attain near equilibrium states could be delineated and were not critical.

Characterization of final states

From a design point of view a major remaining unresolved problem appeared to be the prediction of the final stable state. Merrill and Jorden (1975) have reported that it is possible to predict the final "equilibrium" states attained by lime-treated waste waters by employing equilibrium theory and substituting experimentally determined "activity product constants" for the thermodynamic solubility product values. They demonstrated that predictions based on these assumptions are in excellent agreement with experimental values for lime-treated raw sewage. A disadvantage of the Merrill and Jorden approach is its complexity : the need for a complete raw water analysis,

e.g. Ca, Mg, Na, K, Cl, SO_4, NO_3, PO_4, total alkalinity and NH_3, as well as pH and temperature, and selected treated water analyses to identify all the dissolved species; experimental determination of the relevant activity product constants for each specific waste water; and complex computer computations for making the actual predictions. Therefore, if their approach is to be utilized for design purposes, fairly sophisticated analytical and computer facilities are a prerequisite. In this investigation it was attempted to find a technique for the prediction of the final states attained by lime-treated waste waters which does not require the high degree of sophistication associated with the Merrill and Jorden approach. For this purpose the graphical technique developed by Loewenthal and Marais (1976), referred to as the Modified Caldwell-Lawrence Diagram, was used. The Diagram is based on the equilibrium theory of the calcium-magnesium-carbonic-water system. Solution of an equilibrium problem using this Diagram requires an analysis only of the raw water Ca, Mg, total alkalinity, pH, temperature and total dissolved solids.

Before attempting to predict final states attained by lime-treated waste waters, the validity of Diagram predictions for pure synthetic $CaCO_3$-$Mg(OH)_2$ solutions simulating lime-treated secondary effluent was tested. Diagram predictions for the three basic treated effluent characterizing relationships, i.e. residual calcium versus pH, residual total alkalinity versus pH and lime dosage versus pH, were all in fair agreement with experimental results. However, it was noted that experimental Ca_T^{2+}, Mg_T^{2+}, Alkalinity and lime dosage values for the pH range studied were slightly greater than the predicted values. Four possible reasons for these discrepancies were considered,

(1) neglecting ion pairing, particularly the ion pairs $CaOH^+$ and $CaCO_3^o$,

(2) neglecting the effect of magnesium on the thermodynamic solubility product for calcite,

(3) inaccuracies in pH measurements, and

(4) thermodynamic equilibrium had not been attained.

To overcome problems associated with (1) and (2) above new Modified Caldwell-Lawrence Diagrams were drawn incorporating ion pairs $CaOH^+$, $CaCO_3^o$, $CaHCO_3^+$, $MgOH^+$, $MgCO_3^o$ and $MgHCO_3^+$, and the effect of a range of hypothetical $CaCO_3$ solubility product values. The predictions for the three basic characterizing relationships from such a new Diagram were in good agreement with the experimental results. These results indicate the validity of applying the simple graphical technique, i.e. the Modified Caldwell-Lawrence Diagram with incorporated ion pairing effects and the effect of magnesium on the calcite solubility product, for predicting pure synthetic $CaCO_3$-$Mg(OH)_2$ system final states.

Lime-treated secondary effluent and settled sewage were characterized in a number of batch experiments. The basic characterizing relationships, i.e. pH versus lime dosage, alkalinity, and residual total dissolved calcium and magnesium, for these two effluents were very similar. It was found possible to predict experimental results within 0-20 percent of the measured results by using a Modified Caldwell-Lawrence Diagram with $pK_{CaCO_3} = 6,70$ and $pK_{Mg(OH)_2} = 10,70$.

A problem was encountered with the prediction of lime demand, i.e. the measured lime demand was consistantly higher ($\pm$ 27 percent) than the predicted lime demand. The reasons for this discrepancy are thought to be due to,

(1) the lime demand of effluent phosphates,
(2) ammonia,
(3) organic matter,
(4) sludge, and
(5) incomplete lime dissolution.

Although the effects of (1) and (2) were quantified, the effects of (3) to (5) could not be quantified except by using an approximate equality for predictive purposes, i.e.

$$LD_E \simeq 1,27 \times LD_P \quad \ldots\ (R.5)$$

where LD_E = experimentally measured lime demand (mg ℓ^{-1} as $CaCO_3$)
LD_P = predicted lime demand. (mg ℓ^{-1} as $CaCO_3$)

Applying the Diagram (with $pK_{CaCO_3} = 6,70$ and $pK_{Mg(OH)_2} = 10,70$) developed for Pretoria Sewage Works lime-treated secondary effluent to literature reported results for a lime-treated secondary effluent of different origin resulted in excellent predictions of the reported Ca_T^{2+} and Mg_T^{2+} versus pH relationships. Applying the Diagram to literature reported data for lime-treated raw domestic sewage resulted in a predicted Ca_T^{2+} versus pH relationship significantly lower than the measured relationships. The reason for this discrepancy is thought to be due to incomplete calcium carbonate precipitation, because of the absence of recirculated sludge in this particular reaction system. Alternatively, the effluent is not characterized by $pK_{CaCO_3} = 6,70$, as in the case of lime-treated settled sewage from the Pretoria Sewage Works, but is characterized by a different pK_{CaCO_3} value, i.e. $pK_{CaCO_3} = 6,30$. From these observations it is evident that before the Diagram can be generally applied it will first be necessary to test Diagram predictions for a large number of lime-treated effluents of different origin and chemical composition.

Full-scale lime treatment

A number of studies were made of the full-scale lime treatment process on the Stander Plant to establish whether the findings of the laboratory studies are applicable to full-scale systems. The following specific objectives were pursued,

(1) To evaluate $CaCO_3$ and $Mg(OH)_2$ precipitation in full-scale reaction systems, with and without sludge recirculation, for a range of lime dosage rates and at different CSTR residence times.

(2) To obtain the optimum configuration and operating conditions for the Stander Plant lime treatment process reactor-clarifier system.

(3) To establish if the quality of lime treatment process effluent can be predicted using the Modified Caldwell-Lawrence Diagram.

Full-scale lime reactor effluent was unstable when the reactor was operated without sludge recirculation to a point prior to the reactor. The unstable effluent precipitated upto 25 mg ℓ^{-1} (as $CaCO_3$) calcium carbonate and 31 mg ℓ^{-1} (as $CaCO_3$) magnesium hydroxide. This observation is consistant with similar observations made during the laboratory bench-scale CSTR studies of lime-secondary effluent reactions in the absence of inoculated sludge, i.e. the slow secondary phase precipitation phenomenon is evident.

The most effective process configuration for lime treatment on the Stander Plant was a reactor-clarifier combination with sludge recirculation to a point prior to the reactor. This mode of operation resulted in the lowest residual calcium and magnesium concentrations in the clarifier effluent for any specific pH value. The beneficial effect of the point of sludge discharge prior to the reactor and the maintenance of a sludge blanket in the clarifier, is mainly to be noted in magnesium removal. Magnesium precipitation to "equilibrium" also appears to be the deciding factor in the choice of residence times and sludge age.

Increasing the lime reactor and sludge blanket clarifier residence times and sludge age by a factor of two did not result in significantly increased calcium or magnesium removal, as compared to removals at the standard residence times and sludge age. Reactor and clarifier residence times of 10,8 and 60 minutes, respectively, and a sludge age of about 3 to 5 days, appear to be sufficient to give effluents stable with respect to Ca_T^{2+} and Mg_T^{2+}. It is concluded that near stable effluent, which will not give rise to significant post clarifier precipitation or scale formation, can be produced on the Stander Plant using the above described optimal process configuration and standard reactor

and clarifier residence times and sludge age.

Significant long-term scaling problems at clarifier weirs, troughs and in the pumps and pipes transporting the treated effluent were observed on the Stander Plant even when operating the lime treatment process according to the optimal process configuration. It was concluded that these scaling problems are primarily due to the absorption of small quantities of carbon dioxide at the clarifier surface, overflow weir and collection trough. It was suggested that the problem could be overcome or minimized by suitably covering clarifier weirs and troughs to minimize carbon dioxide absorption opportunaty. Another alternative is to make use of open ducts and gravity flow instead of pipes and pumps, in this manner making the scale which will inevitably form readily accessable for mechanical cleaning.

The relationships between pH and residual calcium and magnesium concentrations for clarifier effluent were predicted using a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 6,7 and $pK_{Mg(OH)_2}$ = 10,5. Clarifier effluent quality data was collected for operation with influent quality which varied significantly and lime treatment which was varied to result in clarifier effluent pH values in the range 10,8 to 11,4. The Diagram-predicted relationships were in good agreement with the measured relationships when operating according to the above indicated optimal process configuration. The successful application of the Diagram for the prediction of full-scale process effluent quality gives greater credibility to this predictive technique, which has so far in this investigation only been tested on batch experimental results.

One of the observations made during the evaluation of the Stander Plant lime treatment process which was subsequently turned to benefit, was that the air sparging mixing system used in the lime reactor resulted in significant quantities of carbon dioxide being absorbed by

the alkaline effluent from the air used for mixing by the sparging system. This resulted in ineffective use of lime and increased the sludge generation rate. It was recommended that the air sparging mixing system be replaced by a mechanical stirrer. This recommendation was subsequently implemented with concomitantly more effective lime usage and lower sludge generation rates.

Apparent solubility products

As previously indicated, the Modified Caldwell-Lawrence Diagram was accepted as a model for characterizing lime-treated effluent. The pK_{CaCO_3} and $pK_{Mg(OH)_2}$ values utilized for fitting model predictions to experimental data were selected by a process of trial and error. The fact that reasonable correlation between predicted and experimental results could be obtained, indicated that perhaps these pK values are real constants reflecting the influence of contaminants on the thermodynamic constants. If it could be shown that activity products for $CaCO_3$ and $Mg(OH)_2$ for "near" stable lime-treated effluents were similar to the K_{CaCO_3} and $K_{Mg(OH)_2}$ values used in the Diagram to give good predictions, a rational basis would be available for the application of the Diagrams to problems related to lime-treated secondary effluent. To ascertain if activity products and Diagram apparent solubility product values are in fact similar, a study was made of $CaCO_3$ and $Mg(OH)_2$ activity products for lime-treated secondary effluents and recarbonated effluents.

Experimentally determined calcium carbonate activity product values for lime-treated secondary effluent were found to change with time, even after long reaction periods. However, changes in activity product values after reaction periods of 24 hours were minimal and for practical purposes these activity product values can be considered constant. The $CaCO_3$ activity product constant values were independent of pH and temperature for the experimental conditions studied in this investigation, i.e. pH in the range 9,8 to 11,7 and temperature in the range 8 to 23°C. The average $CaCO_3$ activity product constant value was $10^{-6,8}$.

Initially it was concluded that experimentally determined calcium carbonate activity product values for recarbonated effluents are a function of pH. However, it was demonstrated that this is not the case, but that the $CaCO_3$ activity product values are in fact constant, at approximately $10^{-7,1}$. The apparent pH dependence of the activity product arose as a consequence of recarbonation to undersaturated conditions, which resulted in concomitant decreases in the $CaCO_3$ activity product values with decreasing pH values.

Magnesium hydroxide activity product values for lime-treated secondary effluent also displayed a dependence on pH. Merrill (1974) reported similar observations for lime-treated raw domestic sewage. However, it was demonstrated that the apparent activity product dependence on pH is a result of incomplete precipitation. When magnesium hydroxide was precipitated in the presence of high concentrations of sludge and sufficient reaction time was allowed, $Mg(OH)_2$ activity product values were found to be independent of pH. The average $Mg(OH)_2$ activity product constant for pH values in the range 10,8 to 11,4 and a temperature of approximately 20°C, is $10^{-10,5}$.

The average values for $CaCO_3$ and $Mg(OH)_2$ activity product constants for lime-treated secondary effluent, $10^{-6,8}$ and $10^{-10,5}$ respectively, were in good agreement with the K_{CaCO_3} and $K_{Mg(OH)_2}$ values found by trial and error in fitting Modified Caldwell-Lawrence Diagram predictions to experimental values, $10^{-6,7}$ and $10^{-10,5}$, respectively. This reasonable agreement between experimental activity product constants and Diagram K values assures a rational basis for the application of the Modified Caldwell-Lawrence Diagram to problems related to lime-treated secondary effluent.

Design guidelines

This investigation on $CaCO_3$ and $Mg(OH)_2$ precipitation pinpointed many of the causes of the problems which in the past have resulted in non-optimal design of precipitation processes in reclamation plants. Based on this new information, process design guidelines for lime

treatment and recarbonation processes are set out with particular attention being given to the design sequence and the decisions which must be made at each step within this sequence. The application of the design guidelines is illustrated by a detailed example of a process design for a full-scale lime treatment plant.

The Diagram with $pK_{CaCO_3} = 6,7$ and $pK_{Mg(OH)_2} = 10,5$, used for design predictions, was specifically developed for lime-treated secondary effluent where the effluent was derived from a waste water treatment plant treating domestic sewage. Should the waste water originate from an industrial source, it should be realised that the Diagram may not give good predictions due to the presence of foreign sequestering and complexing agents which may alter the values of pK_{CaCO_3} and $pK_{Mg(OH)_2}$.

Recommended future research

This investigation has brought to light a number of aspects related to $CaCO_3$ and $Mg(OH)_2$ precipitation which require further research,

(1) The applicability of the Modified Caldwell-Lawrence Diagram should be established for a wide range of lime-treated waste waters with different Ca_T^{2+}:Mg_T^{2+}:Alkalinity ratios. These differences in quality may be due to variations within the same waste water source or waste water from different origins. The pK_{CaCO_3} and $pK_{Mg(OH)_2}$ values should be determined for a range of temperatures.

(2) The problem of intermediate and final stability of reclaimed water after lime treatment and recarbonation should be investigated, i.e. how do processes such as chlorination and carbon adsorption effect the solubility of calcium carbonate in reclaimed effluent and what happens to an apparently stable final effluent during long residence times in water reticulation systems.

(3) Equipment design features for minimizing carbon dioxide absorption at the clarifier weirs and troughs should be investigated at full-scale level. The investigations should stretch over relatively long periods since it is the long-term scale formation effects which must be evaluated.

(4) The three suggested methods for achieving optimum lime dissolution, i.e. split stream treatment, recycle stream treatment and main stream treatment using in-line static mixing, should be tested at the pilot- or full-scale level to ascertain which method or combination of methods gives the best results, considering both overall costs and final effluent quality.

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NOTATION

A = area

A' = constant

ACID. = total acidity (mg ℓ^{-1} as $CaCO_3$)

$ACID_{HTE}$ = total acidity (mg ℓ^{-1} as $CaCO_3$)

ALK. = total alkalinity (mg ℓ^{-1} as $CaCO_3$)

AMRT = average mean residence time (min)

AP(X) = activity product of compound X

B^o = nucleation rate

C = concentration (mol ℓ^{-1}) at time t = t

C_i = concentration (mol ℓ^{-1}) of the ith ion

C_m = concentration (mol ℓ^{-1}) at time t = infinity

C_o = concentration (mol ℓ^{-1}) at time t = o

C_T = total carbonic species (mol ℓ^{-1})

$[Ca^{2+}]$ = free ionic calcium concentration (mol ℓ^{-1})

$[Ca_T^{2+}]$ = residual total dissolved calcium (mol ℓ^{-1})

$CaCO_3(ppt)$ = calcium carbonate precipitated (mg ℓ^{-1})

$CaCO_3(s)$ = concentration of $CaCO_3$ suspended in solution (mg seed ℓ^{-1})

$Ca_3(PO4)_2(ppt)$ = tricalcium phosphate precipitated (mg ℓ^{-1})

CO = clarifier overflow

$CO_2(RE)$ = carbon dioxide reacted with effluent (mg ℓ^{-1} as $CaCO_3$)

COD = chemical oxygen demand (mg ℓ^{-1} as O)

d = diamter

$\frac{d[Ca_T^{2+}]}{dt}$ = rate of change in total dissolved calcium (mol ℓ^{-1} min^{-1})

E = activation energy (kcal mol^{-1})

E.F. = effluent flow rate (ℓ min^{-1})

Exp. = experimental values

f_D = activity factor for divalent ions

f_m = activity factor for monovalent ions

f_x = activity factor for ionic species x

G = temporal mean velocity gradient (m sec^{-1} m^{-1})

h = height

HRT = hydraulic retention time (min)

HTE = humus tank effluent

I = ionic strength of solution (mol ℓ^{-1})

k = proportionality constant (min^{-1})

k_c = rate constant for magnesium hydroxide crystal growth (ℓ mg^{-1} h^{-1})

k_G = rate constant for $CaCO_3$ crystal growth (ℓ mol^{-1} min^{-1})/(mg seed ℓ^{-1})

K = mass action or equilibrium constant

K_{CaCO_3} = solubility product for calcium carbonate (mol^2 ℓ^{-2})

$K_{CaCO_3^o}$ = dissociation constant for $CaCO_3^o$

K_{CaHCO_3} = dissociation constant for $CaHCO_3^+$ (mol ℓ^{-1})

K_{CaOH^+} = dissociation constant for $CaOH^+$ (mol ℓ^{-1})

$K_{CO_3^{2-}}$ = dissociation constant for HCO_3^{2-} (mol ℓ^{-1})

$K_{Mg(OH)_2}$ = solubility product for magnesium hydroxide (mol^3 ℓ^{-3})

K_{sp} = solubility product

K_w = dissociation constant for water (mol^2 ℓ^{-2})

K_1 = dissociation constant for H_2CO_3 (mol ℓ^{-1})

K_2 = dissociation constant for HCO_3^- (mol ℓ^{-1})

L = mean partical size (μm)

LC = lime consumption (kg d^{-1})

L.S.F. = lime slurry flow rate (ℓ min^{-1})

Mg^{2+} = free ionic magnesium ion concentration (mol ℓ^{-1})

Mg_T^{2+} = residual total dissolved magnesium concentration (mol ℓ^{-1})

n = order of reaction

NH_3-N = ammonia nitrogen concentration (mg ℓ^{-1} as N)

Obs. = observed values

p[APC(x)] = negative logarithm of the activity product constant for compound X

pK = negative logartihm of K

pK_x = negative logarith of dissociation constant K_x for species X = H_2CO_3, HCO_3^-, $CaSO_4^o$, $NaSO_4^-$, $MgSO_4^o$, HCD_3 $NaHCO_3^o$, $NaCO_3^-$, $MgHCO_3^+$, $MgCO_3^o$, $CaHCO_3^+$, $CaCO_3^o$, $MgOH^+$, $CaOH^+$, H_2O.

PO_4-P = ortho-phosphate concentration (mg ℓ^{-1} as P)

Pred. = predicted values

Q_E = clarifier effluent flow rate (ℓ min^{-1})

Q_i = influent flow rate (ℓ min^{-1})

Q_L = lime slurry flow rate (ℓ min^{-1})

Q_T = clarifier influent flow rate ($\ell\ min^{-1}$)

Q_r = clarifier underflow flow rate ($\ell\ min^{-1}$)

r = radius

R = gas constant ($kcal\ mol^{-1}\ {}^{o}K^{-1}$)

R_H = hydraulic retention time (min)

R_S = sludge age (days)

RE = reactor effluent

RS = recycled sludge stream

S = surface area term

t = time (min)

$\bar{t}$ = mean residence time (min)

T = absolute temperature (^{o}K)

T_c = temperature (^{o}C)

T_k = temperature (^{o}K)

V = volume

VS = volatile solids ($mg\ \ell^{-1}$)

x = molar fraction of magnesium in magnesian-calcite

X_i = steady state sludge concentration in clarifier influent (g ℓ^{-1})

X_r = steady state sludge concentration in clarifier underflow (g ℓ^{-1})

Z_i = ionic charge of the ith ion in solution

$\frac{\delta[CaCO_3]}{\delta t}$ = rate of change in total calcium carbonate concentration (mole ℓ^{-1} min^{-1})

ΔG = standard free energy change

ΔH = enthalphy change

( ) = activity of enclosed species (mol ℓ^{-1})

[ ] = concentration of enclosed species (mol ℓ^{-1})

$[\ ]_{eq}$ = equilibrium concentration of enclosed species (mol ℓ^{-1})

$[\ ]_{\infty}$ = concentration at time infinity of enclosed species (mol ℓ^{-1})

{ } = degree of supersaturation (mol^2 ℓ^{-2})

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AUTHOR INDEX

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CHAPTER 1

GENERAL INTRODUCTION

The harmful effects of industrial and domestic waste waters on the utilization of water resources have aroused a world-wide awareness of the need for water pollution abatement. Reclamation of effluents, re-use of water and closed-circuit water utilization are some of the methods currently being applied in South Africa for water conservation and pollution control (Stander and Van Vuuren, 1969).

One of South Africa's best known contributions to research in the field of water pollution abatement is her research in the field of potable water reclamation from secondary effluents. Through her efforts the world's first and only water reclamation works treating maturation pond effluent to potable water standards for *domestic use*, was designed, constructed and is still being operated in the City of Windhoek, South West Africa.

The reclamation of waste waters comprises the removal of a wide range of pollutants to restore the original quality of the water (Cillié, 1975). According to the nature of these pollutants, advanced technological processes have been developed based on biological, physical and chemical principles used either singly or in combination. The various renovative processes are essentially concerned with the removal of nitrogen, phosphorous, organic carbon, dissolved minerals, heavy metals, pathogens and toxicants. The selection of a particular advanced treatment process is to a large extent dependent on the character of the raw water and the quality requirements for the specific uses envisaged.

Most of the process configurations that have been proposed for waste water reclamation include the addition of lime to some pH value to induce coagulation of colloidal matter, flocculation of coagulated and suspended organic matter and precipitation of phosphates. Usually

a pH higher than 11,0 is required for adequate clarification of lime-treated effluent, utilizing the natural flocculation properties of magnesium hydroxide present in the effluent. This treatment is referred to as the High Lime process. The process is employed in the full-scale reclamation plants in Pretoria (South Africa) and Windhoek (South West Africa). In the Pretoria plant the sequence of unit processes is as follows : high lime treatment, quality equalization, ammonia stripping, recarbonation, sand filtration, breakpoint chlorination, activated carbon treatment, and final stabilization and chlorination. Similar unit processes are utilized for reclaiming treated waste effluents at Lake Tahoe (United States of America) and at the Dan Region Project (Israel).

Optimum design of reclamation plants is hampered by a lack of fundamental knowledge of the processes involved. One of the areas of ignorance is a detailed knowledge concerning inorganic precipitation - the speed at which precipitation takes place and the final equilibrium states which are attained. In the high lime and recarbonation processes supersaturated conditions cause calcium carbonate and magnesium hydroxide precipitation in reactors and in subsequent process units and pipes transporting the effluent. This causes serious practical problems of flow reductions, blockages in pipes, seizure of pumps and mudball formation in sandfilters.

Precipitation reactions pose two fundamental problems,

(1) What should be the residence times and reactor configurations to ensure a virtually stable water? This is a kinetic problem involving rates of precipitation.
(2) What constitutes a stable water, i.e. a water that will not give rise to post-precipitation? This is a classical equilibrium problem.

Reported research into the precipitation kinetics and equilibrium chemistry of calcium carbonate has concentrated primarily on synthetic "pure" or defined systems, i.e. systems containing analytical reagent grade salts, e.g. calcium chloride and sodium carbonate. A

number of studies have also been published on the effect of individual substances on the rate of precipitation and solubility of pure calcium carbonate. Typical examples are studies of the influence of magnesium ions, phosphorous compounds and organic matter. Some of these substances have significant effects on the rate of precipitation and the final equilibrium state of solutions of calcium carbonate.

Models for calcium carbonate precipitation kinetics have been proposed in the literature. However, there is some doubt whether these models are applicable to the lime treatment and recarbonation processes, since they are based on experimental data obtained under conditions very different from those reigning in these processes, particularly with respect to calcium and carbonate ion- and precipitated $CaCO_3$ concentrations. It is also evident that the following substances which are commonly present in sewage effluents, i.e. phosphorus in all its forms, organic material and magnesium, acting either separately or in conjunction, affect $CaCO_3$ precipitation. The results may differ by orders of magnitude from those predicted by "pure" system experiments.

From a research point of view, the wide scope of this subject poses a dilemma. On the one hand a fundamental approach to the problem implies a massive research effort over an unknown period to delineate $CaCO_3$ precipitation kinetics, "pure" equilibrium states, the effect of each of a number of influencing factors (some still unknown) and their conjoined effects. On the other hand, the urgency of the problem and the economic factors to be considered for plants soon to built require some rational criteria for design which will allow plant optimization.

This investigation commenced by taking the first or fundamental point of view. However, it soon became apparent that this approach would contribute little to the criteria for design in the time available to obtain solutions suitable for application in design.

After a thorough re-appraisal of the situation, and in particular taking into consideration the urgency to find practical solution procedures (as voiced by the engineers), it was decided to redirect the investigation in accordance with the second point of view. The approach then taken was : If the basic phenomena of precipitation of $CaCO_3$ and $Mg(OH)_2$ from pure solutions can be modelled satisfactorily, these models can serve as a basis for modelling the heterogeneous systems by appropriately changing the pure system constants to fit the results from operating plants. Inevitably such an approach introduces an element of empiricism into the model ; the usefulness and success of the model will depend on whether it is possible to obtain consistency in prediction for similar types of effluent at different plants.

Since no satisfactory model was available to describe the precipitation kinetics of calcium carbonate in "pure" systems under conditions which simulate those prevailing in the high lime treatment and recarbonation processes, an endeavour was made to obtain such a model. Once this was achieved, precipitation in heterogeneous systems was investigated and modelled on the basis of the "pure" system model.

As an apparently satisfactory model for magnesium hydroxide precipitation was already available from the literature, no further $Mg(OH)_2$ "pure" system investigations were made. This model was accepted as a basis for modelling $Mg(OH)_2$ precipitation from heterogeneous effuents. Similarly, "pure" system precipitation kinetics for phosphates are well established and no further work on this system was deemed necessary. Pure system studies of organic material removal from solution were not considered since the composition of the organic material in sewage effluent is a virtually unexplored field and considered outside the scope of this thesis.

In Chapter 2 the literature of both synthetic and heterogeneous calcium carbonate and magnesium hydroxide systems is reviewed. Aspects related to precipitation kinetics and equilibrium states are emphasized.

Chapter 3 deals with synthetic system calcium carbonate precipitation in batch and continuous precipitation reactors.

Chapter 4 deals with laboratory studies of lime-secondary effluent reactions and characterization of final states.

Chapter 5 deals with precipitation studies on the full-scale Stander Water Reclamation Plant.

Chapter 6 deals with equilibrium studies of the $CaCO_3$ and $Mg(OH)_2$ systems.

Chapter 7 details process design procedures for calcium carbonate and magnesium hydroxide precipitation, the lime treatment process and calcium carbonate precipitation in the recarbonation process.

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CHAPTER 2

LITERATURE SURVEY

1. INTRODUCTION

This literature survey has as its prime objective the establishment of the status of the knowledge in the various fields of science and technology utilized in the lime treatment process for water reclamation. Aspects reviewed are : Fundamental principles underlying equilibrium behaviour and application of these principles to calcium carbonate and magnesium hydroxide systems; fundamental principles of nucleation and crystal growth kinetics and their application to the precipitation kinetics of calcium carbonate and magnesium hydroxide; effects of phosphates, magnesium and organic matter on calcium carbonate equilibria and precipitation kinetics; lime treatment of surface-, ground- and waste waters at laboratory, pilot and full scale plant level; design guidelines for the lime treatment process.

At the present stage of development of water renovation processes, it is often difficult to form an opinion from the papers reported in the literature as to which aspects of precipitation kinetics and equilibria are relevant and important. No critical survey exists in which a detailed analysis of the research work published has been made and the importance and relevance of these research results assessed with respect to water reclamation. The survey presented here will attempt to do so and for this reason some of the papers reviewed may appear irrelevant. Although these papers may not be pertinent to the specific topic of this thesis, they are included to make it as comprehensive a review as possible of precipitation kinetics and equilibria of the $CaCO_3$ and $Mg(OH)_2$ systems.

2. EQUILIBRIUM BEHAVIOUR

2.1 General

In an aqueous solution at equilibrium, the activities of the chemical species present are related by a set of mass action equilibrium equations (Truesdell and Jones, 1973) of the form,

$$aA + bB \rightleftharpoons cC + dD \quad \ldots\ldots (2.1)$$

in which lower case letters represent the stoichiometric coefficients of the chemical species represented by the upper case letters. The mass action equation is of the form,

$$\frac{(C)^c(D)^d}{(A)^a(B)^b} = K \quad \ldots\ldots (2.2)$$

In this equation, K is the mass action or equilibrium constant and the brackets represent activities, i.e. active mass concentrations.

Equilibrium constants may be derived from experimental measurement of species concentrations in a series of equilibrated solutions of different total concentration by extrapolation to infinite dilution. Alternatively, the experimental concentrations may be corrected to activities by means of calculated activity coefficients and the value of K calculated. Equilibrium constants for a reaction may also be derived from the standard free energy change of that reaction. For example in the reaction given by Eq. (2.1), the standard free energy change, ΔG, is defined as the sum of the standard free energies of formation of the

products multiplied by their stoichoimetric coefficients, less the sum of the standard free energies of formation of the reactants multiplied by their stoichiometric coefficients, i.e.

$$\Delta G^{o}_{r} = c.\Delta G^{o}_{f},C + d.\Delta G^{o}_{f},D - (a.\Delta G^{o}_{f},A + b.\Delta G^{o}_{f},B) \quad \ldots\ (2.3)$$

where $\Delta G_{f},X$ is the standard free energy of formation of reactants and products, X.

The standard free energy of reaction is related to the equilibrium constant of the reaction, K, by the equation,

$$\Delta G^{o}_{r} = -2,303\ RT \log K \quad \ldots\ (2.4)$$

where R = universal gas constant (cal $mol^{-1}{}^{o}K^{-1}$)
T = absolute temperature (^{o}K)

By means of these equations, experimental equilibrium data may be related to thermochemical data derived from calorimetric measurements.

The great majority of experimental determinations of equilibrium constants and standard free energy values have been made at 25°C. If experimental values are available over a range of temperatures, or, if complete thermochemical data is available for all species of a reaction, then the equilibrium constant may be expressed as a function of the absolute temperature. Where values of the equilibrium constant are available for a range of temperatures, one of the functional forms is,

$$\log K = A + B.T + C/T + D.\log T \quad \ldots \quad (2.5)$$

in which one or more coefficients (A,B,C,D) may be zero. If experimental determinations at only two or three temperatures are available, only a linear dependence of log K with the reciprocal of the absolute temperature can be derived. This is equivalent to accepting a constant value for the enthalpy (heat content) change of the reaction, ΔH. This approximation is inherent in the Van't Hoff relationship,

$$\log K = \log K_{Tr} - \frac{\Delta H_{Tr}}{2.3R} \{\frac{1}{T} - \frac{1}{Tr}\} \quad \ldots \quad (2.6)$$

where Tr = reference temperature (say 298,15°K (25°C))

K_{Tr} = equilibrium constant at Tr

ΔH_{Tr} = enthalpy change of reaction at Tr

and the constants A and C in Eq. (2.5) are

$$A = \log K_{Tr} + \frac{\Delta H_{Tr}}{2,3RT}$$

and

$$B = \frac{\Delta H_{Tr}}{2,3R}$$

respectively.

The equilibrium of a solid phase with an aqueous solution also can be characterised by a mass action equation. For a solid, represented by the functional formula AX, which dissolves to form ions A^+ and X^-, this equation is,

$$\frac{(A^+)(X^-)}{(AX)} = K \quad \ldots\ (2.7)$$

where K is the solubility equilibrium constant. If the solid is a pure substance, not a solid solution, its activity is equal to one because it is in its standard state (by definition) and the expression for the equilibrium constant reduces to the "solubility product", K_{sp},

$$(A^+)(X^-) = K_{sp} \quad \ldots\ (2.8)$$

The standard enthalpy of formation and standard entropy for most solids (minerals) have been determined by means of calorimetric methods. These two quantities are used for the calculation of standard free energies of formation of elements rather than ions formed in the solutions of the mineral. The combination of such standard free energy values with those for solution species involving aqueous ions, may lead to erroneous equilibrium constants (when using Eq. 2.4). The use of experimental solubility products is free from such inconsistancies. The main uncertainty in the use of experimental solubility products lies in the precise description of the reactants and products involved in the experiment and the problem of incongruent precipitation.

A more rigorous treatment of solid-liquid-equilibria may be found in a standard text on the subject by Haase and Schonert (1969).

2.2 $CaCO_3$ Solubility Product

The thermodynamic solubility product for calcium carbonate, $K_{sp_{CaCO_3}}$*, is defined by the following equations (Nancollas and Reddy, 1971),

$$(Ca^{2+})(CO_3^{2-}) = K_{CaCO_3} \quad \ldots\ (2.9)$$

or

$$[Ca^{2+}].f_{Ca^{2+}}.[CO_3^{2-}].f_{CO_3^{2-}} = K_{CaCO_3} \quad \ldots\ (2.10)$$

where ( ) = free ion activities (mol ℓ^{-1})

[ ] = free ion concentrations (mol ℓ^{-1})

f_x = activity factor for ion X

Calcite is the thermodynamically stable form of calcium carbonate at ambient temperature and atmospheric pressure. A number of different experimental techniques have been used to determine solubility product values for calcite. Frear and Johnston (1929), Shternina and Frolova (1952), and Yanat'yena (1954) utilized partial pressure of carbon dioxide and dissolved calcium concentration measurements and determined pK_{CaCO_3} to be 8,40 $\pm$ 0,02. Garrels, Thompson and Siever (1960) utilized partial pressure of carbon dioxide and pH measurements and determined a value of 8,44 $\pm$ 0,06. Grezes and Basset (1965) utilized pH and dissolved calcium measurements and determined a value of 8,35 $\pm$ 0,02. A recent estimate of pK_{CaCO_3} for calcite at 25°C and one atmosphere pressure is 8,40 $\pm$ 0,02 (Langmuir, 1968).

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*For simplicity $K_{sp_{CaCO_3}}$ will be referred to as K_{CaCO_3} throughout this thesis. This abbreviation should not be confused with the dissociation constant for the calcium carbonate ion pair, $K^{o}_{CaCO_3}$.

Solubility products determined by the three different techniques all show good agreement with one another, i.e. all the pK_{CaCO_3} values lie within the narrow range of 8,35 to 8,44. For practical application a value of 8,37 as given by Truesdell and Jones (1973) (see below) is sufficiently close to all the experimentally determined values.

The temperature dependence of the calcium carbonate solubility product was determined by Larson and Buswell (1942). They used data collected by Frear and Johnston (1929) and other investigators and determined the solubility product for unit activity for pure systems in the temperature range $0^{o}C$ to $80^{o}C$. A graphical plot of their data yields the following relationship (Loewenthal and Marais, 1976),

$$pK_{CaCO_3} = 0,01183.T_c + 8,03 \quad .... \quad (2.11)$$

where T_c = temperature (^{o}C)

Truesdell and Jones (1973) predicted the temperature dependence of pK_{CaCO_3} from thermodynamic considerations, i.e.,

$$pK_{CaCO_3} = 10,710 - 698,61/T_k \quad .... \quad (2.12)$$

where T_k = temperature (^{o}K)

Predictions by Eqs. (2.11) and (2.12) are compared in Table 2.1. Although the predictions are very similar, those of Truesdell and Jones (1973) are closer to the value at $25^{o}C$ reported by Langmuir (1968) and therefore perhaps more acceptable.

Table 2.1

Predicted pK_{CaCO_3} - temperature dependence

Temperature		pK_{CaCO_3}	
^oC	^oK	Loewenthal & Marais	Truesdell & Jones
10	283	8,15	8.24
20	293	8,27	8,32
25	298	8,33	8,37
30	303	8,39	8,40

The calcium carbonate solubility product has practical importance in predicting scaling properties of water for domestic and industrial purposes. The pioneer in this field was Langelier (1936). He introduced the pH_s concept, that is, the pH at which a particular water is in equilibrium with calcium carbonate. K_{CaCO_3} values used by Langelier in his pH_s formula were later shown by De Martini (1939) to give satisfactory qualitative predictions of scaling behaviour of drinking water in reticulation systems. Ryznar (1944) proposed a modified scaling index which he claimed to be a quantitative measure, although it is in fact only a linear function of Langelier's saturation pH. Caldwell and Lawrence (1953) presented a method based on equilibrium relationships for predicting changes in water quality, i.e. pH, alkalinity, calcium concentration and precipitation potential, by means of a conditioning diagram. Loewenthal and Marais (1976)

refined this conditioning diagram by introducing the concept of acidity, thereby rationalizing and simplifying the application of the diagram to the solution of problems. Their "Modified Caldwell-Lawrence Diagram" may be used for obtaining solutions to problems relating to chemical conditioning of waters considering equilibrium states in the aqueous phase, aqueous and solid phases, or aqueous, solid and gaseous phases. Practical applications include water softening, water stabilization, water blending and CO_2 stripping.

The Modified Caldwell-Lawrence Diagram (Figure 2.1) graphically represents equilibrium inter-relationships between Alkalinity, Acidity, pH and Calcium in a plot with the parameters Acidity and Total Alkalinity-Calcium (Alk-Ca) as coordinates. The Diagram can constitute either a single, two or three phase equilibrium Diagram.

In single phase aqueous systems, any two of the three parameters Alkalinity, Acidity and pH define equilibrium values for the carbonic species in solution. Thus in the Diagram the intersection point of the lines representing the values of any two of these parameters defines the equilibrium value of the third parameter, i.e. plotting the lines representing measured Alkalinity and pH values of a water in the Diagram, the Acidity ordinate value of the intersection point defines the Acidity of the water.

In two phase systems, i.e. solid and liquid phase systems, any three of the four parameters Alkalinity, Acidity, pH and Calcium define equilibrium values for the carbonic and calcium species in solution. In three phase systems, i.e. solid, liquid and gaseous phase systems, any four of the five parameters Alkalinity, Acidity, pH, Calcium and carbon dioxide partial pressure define equilibrium values for the carbonic and calcium species in solution. In the Diagram only one partial pressure of CO_2 is considered, that of CO_2 in the atmosphere.

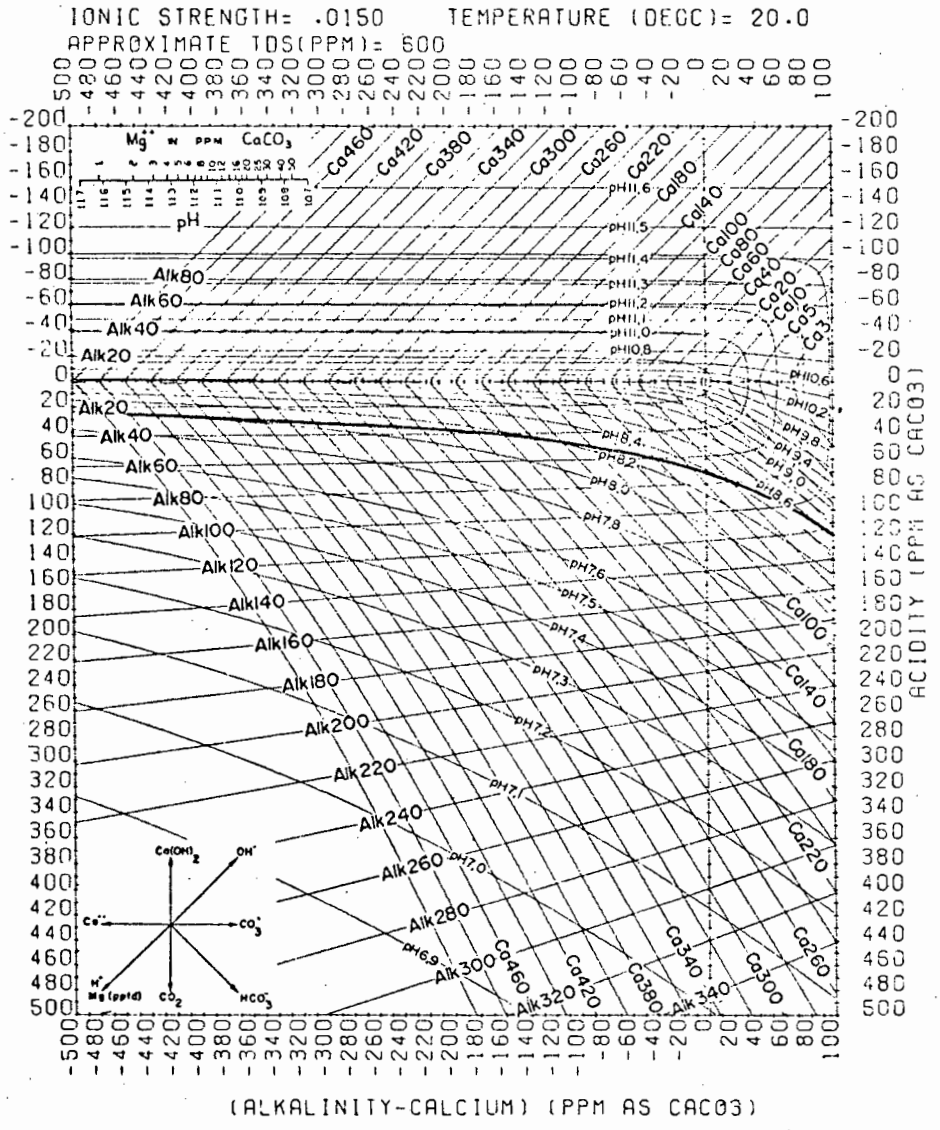

Figure 2.1. A typical Modified Caldwell-Lawrence Diagram (After LOEWENTHAL and MARAIS, 1976)

Numerous examples demonstrating the application of the Diagram to practical problems have been given by Loewenthal and Marais (1976) in their book "Carbonate Chemistry of Aquatic Systems - Theory and Application". Application of the Diagrams in the context of this thesis is illustrated in Appendix 1.

This predictive technique is valid for relatively pure systems as found in water supply operations. However, the following limitations prevent the application without modification of this technique to lime-treated sewage effluents :

(1) Solubility product values for calcite and brucite in the mathematical equations on which this Diagram is based, are not valid for sewage effluents, both treated and untreated,
(2) Ion-pairing effects are not incorporated, and
(3) Alkalinity contributions by phosphates, silicates and ammonia are not included in the Diagram.

2.2.1 Solubility products for heterogeneous systems

In heterogeneous systems such as lime treated sewage effluents, a number of factors other than temperature affect the solubility of calcium carbonate : inorganic compounds such as magnesium (Doner and Pratt, 1969), complex phosphates (Reddy and Nancollas, 1973), tannins, lignins, starches and poly-acrylates (Betz, 1971); parameters such as particle size (Chave and Schmalz, 1966) and the crystallographic forms of the precipitate (Dedek, 1966). The combined effect of these factors gives rise to apparently increased K_{CaCO_3} values for lime-treated waste waters.

For lime-treated secondary effluent Seiden and Patel (1969) established the following relationships,

$$pK_{CaCO_3} = -1,082\ pH + 16,4 \quad ..... \ (pH<9,75) \qquad .... \quad (2.13)$$

and

$pK_{CaCO_3} = 5,89$ ..... (pH 9,75) .... (2.14)

This strong dependence on pH at lower pH values suggests the effluents under consideration were not saturated but in fact undersaturated.

Merrill and Jorden (1974 and 1975) reported apparent pK_{CaCO_3} values for various types of lime-treated effluents (Table 2.2). Their data show that :

(1) Apparent solubility product values are one to two orders of magnitude greater than for the synthetic systems.

(2) The solubility products appear to be roughly proportional to the system waste strength. This relationship is attributed to the inhibiting action of the complex phosphates, since as the complex phosphate concentration increases in the progression from well waters to anaerobic supernatant, the apparent solubility products increase correspondingly.

(3) With lime-treated primary and secondary effluents there appeared to be a dependence of pK_{CaCO_3} on pH values. The dependence, however, is very slight.

Merrill and Jorden (1974 and 1975) determined apparent pK_{CaCO_3} values by taking into account all the ion-pairs that form in significant quantities in lime-treated effluent, in particular, $CaOH^+$, $CaCO_3^o$, $CaHCO_3^+$, $MgOH^+$, $MgCO_3^o$ and $MgHCO_3^+$. Their method of determination was as follows : They developed a computer programme which enabled the calculation of relationships between pH and total dissolved calcium, Ca_T^{2+}. The pK_{CaCO_3} value was adjusted to give the best fit between predicted and experimental Ca_T^{2+}-pH relationships. The pK_{CaCO_3} value so determined is characteristic for the particular system under consideration. This places a limitation on the pK_{CaCO_3} obtained in this fashion, since it only holds for the specific set of conditions it is developed for.

Table 2.2

Experimental pK_{CaCO_3} - values for various lime-treated effluents

(After MERRILL and JORDEN, 1974)

Effluent type	pK_{CaCO_3}
Well water	7,4
Primary and secondary effluent	6,7
Raw waste	6,4
Anaerobic digester supernatant	6,3

One may approach a solution to this problem from a slightly different point of view. Loewenthal and Marais (1977) in their extention of the Caldwell-Lawrence Diagram have provided a computer programme which will plot Diagrams for any selected value of K_{CaCO_3}. This programme also incorporates the relevant ion pairs. A series of Diagrams may be drawn for a set of pK_{CaCO_3} values for preselected ionic strengths and temperatures. The design engineer therefore need not be concerned with the computational aspects, but may select one or a set of Diagrams applicable to his specific problem. An apparent pK_{CaCO_3} for any specific effluent then may be determined as follows : An experimental investigation is made to determine the Ca_T^{2+}-pH relationship for the particular effluent. A set of Diagrams for the appropriate temperature and ionic strength, but

with different pK_{CaCO_3} values are utilized for predicting the Ca_T^{2+}-pH relationship. The predicted relationship which closest fits the experimental relationship will provide the best estimate of the apparent pK_{CaCO_3}.

The proposed approach will be most useful if it can be shown that the approximations inherent in the method have negligable effects on the solution when compared to solutions obtained by the somewhat more rigorous approach of Merrill and Jorden.

2.3 $Mg(OH)_2$ Solubility Product

The thermodynamic solubility product for magnesium hydroxide $K_{sp_{Mg(OH)_2}}$*, is defined by Liu and Nancollas (1973) as,

$$(Mg^{2+})(OH^-)^2 = K_{Mg(OH)_2} \quad \ldots\ (2.15)$$

or

$$[Mg^{2+}].f_{Mg^{2+}}.[OH^-]^2.f_{OH^-}^2 = K_{Mg(OH)_2} \quad \ldots\ (2.16)$$

*For simplicity $K_{sp_{Mg(OH)_2}}$ will be referred to as $K_{Mg(OH)_2}$ throughout this report.

where ( ) = free ion activity (mol ℓ^{-1})

[ ] = free ion concentrations (mol ℓ^{-1})

f_x = activity factor for ionic species, X.

Brucite is the thermodynamically stable form of magnesium hydroxide most commonly found in nature. A survey of reported solubility product values for $Mg(OH)_2$ discloses the following values : Gjaldbaek (1925), reported a $pK_{Mg(OH)_2}$ value of 10,93 (at 18°C) determined by utilizing hydrogen electrode measurements; Nasanen (1941) and Krige and Arnold (1948), determined $pK_{Mg(OH)_2}$ values of 10,74 and 10,85 respectively, using a conductometric method. A recent estimate using this technique is that of Liu and Nancollas (1973), 10,86 $\pm$ 0,03 (at 25°C, one atmosphere). Britton and Robinson (1932) obtained a lower value of 8,70 using a glass electrode titration technique.

The wide disparity in the values reported by Britton and Robinson ($pK_{Mg(OH)_2}$ = 8,70) and the other authors ($pK_{Mg(OH)_2}$ = 10,74 to 10,93) may be explained by the existence of two forms of magnesium hydroxide, first reported by Gjaldbaek (1925). Hamer, Jackson and Thurston (1961) came to the same conclusion, since they also observed two distinctly different forms of magnesium hydroxide. One form ($pK_{Mg(OH)_2} \simeq 9,5$) occurs primarily in precipitates from water treatment processes and is a finely divided barely crystalline meta-stable precipitate. The other form ($pK_{Mg(OH)_2} \simeq 11,9$) is a stable crystalline precipitate.

A number of investigators have determined the temperature dependence of the magnesium hydroxide solubility product experimentally. Other investigators have calculated this relationship from thermodynamic considerations. Travers and Nouvel (1929), the first to determine this relationship experimentally, studied $Mg(OH)_2$ solubility over a temperature range of 35 to 200°C. Carlson, Peppler and Wells (1953) studied $Mg(OH)_2$ solubility in the temperature range 30 to 250°C. Ryznar,

Green and Winterstein (1946) determined a relationship from thermodynamic considerations, as did Truesdell and Jones (1973). The various $pK_{Mg(OH)_2}$ values reported by these researchers are compared in Table 2.3. Hamer *et al* (1961) reported a $Mg(OH)_2$ solubility product-temperature relationship based on the mean of the data of Travers and Nouvel (1929) and Carlson *et al* (1953). Loewenthal and Marais (1976) derived a linear equation for the relationship between $pK_{Mg(OH)_2}$ and temperature based on the data of Hamer *et al* (1961),

$$pK_{Mg(OH)_2} = 0{,}0175T_c + 9{,}97 \quad .... \quad (2.17)$$

where T_c = temperature (^oC)

Comparing the data in Table 2.3 it is clear that there is a wide disparity between both the experimental values and the predicted values. Carlson *et al* (1953) concluded that the solubility varies with the method of $Mg(OH)_2$ precipitation. These authors also agree with Gjaldbaek (1925) that there is an unstable, soluble form of $Mg(OH)_2$ which forms during initial precipitation but eventually recrystallizes to a stable, less soluble form.

The magnesium hydroxide solubility product for heterogeneous systems may be affected by a number of factors other than temperature in the same way as the calcium carbonate solubility product. These factors appear difficult to identify individually so that eventually one may be forced to utilize experimental values obtained for a particular effluent. Merrill (1974) for example reported the following relationship for lime-treated raw sewage,

$$pK_{Mg(OH)_2} = 25{,}537 - 1{,}382.pH \quad .... \quad (2.18)$$

Table 2.3

Literature reported $pK_{Mg(OH)_2}$ - temperature dependence

Temperature	$pK_{Mg(OH)_2}$						
°C	Travers & Nouvel	Carlson *et al*	Ryznar *et al*		Truesdell & Jones	Hamer *et al*	Loewenthal & Marais
			Precipitate	Crystalline			
10	10,64	9,77	9,46	11,90	11,24	10,15	10,15
20	10,67	10,03	9,50	11,88	11,22	10,30	10,32
25	10,71	10,15	9,53	11,87	11,20	10,38	10,41
30	10,75	10,23	9,58	11,86	11,19	10,47	10,50
40	10,84	10,38	9,64	11,87	11,17	10,67	10,67

applicable in the pH range 10,5 to 11,5. The authors could not explain the apparently increased solubility with pH, but speculated that this phenomenon could be accounted for if an appropriate reactive complex could be identified, such as $Mg(OH)_2^o$ or $Mg(OH)_3^-$. It appears unlikely that these proposed reactive complexes do in fact exist, since "ion-groups" with more than two ions, i.e. ion-pairs, are rare and would only be expected under conditions where the contributing ionic species concentration is extremely high. More likely in this pH range under consideration, two crystal forms are precipitated with different pK values, one predominating at the lower pH and the other at the higher pH.

From a practical point of view the most rational approach to predicting magnesium hydroxide solubility is to conduct solubility studies on the specific effluent under consideration. Plant precipitation conditions can be simulated to obtain solubility values under conditions representative of the system under investigation.

3. KINETIC BEHAVIOUR

3.1 General

In water treatment processes such as High Lime Treatment and Recarbonation, inorganic cations and anions, for example calcium, magnesium, carbonate, hydroxide and ortho-phosphate are removed by precipitation. Precipitation involves a phase change from a liquid to a solid phase, a process which is usually time dependent. Sufficient reaction time, and therefore reactor volume(s), must be allowed for the reactions to go to near completion. Hence, knowledge of the kinetics of precipitation of each of the individual precipitation reactions that take place in a specific process is of importance for design purposes.

The precipitation process has two distinct stages, nucleation and crystal growth. In waste water precipitation processes it is usually attempted to minimize nucleation and promote crystal growth. This is achieved by sludge recirculation from the clarification basins to the precipitation reactors, to promote the growth of large crystals. It is undesirable to produce small crystals in precipitation reactors, since small particles settle very slowly and may require the addition of flocculants or flocculant-aids to clarify the liquid.

3.2 Nucleation

The classical theory of nucleation stems from the thermodynamic approach of Gibbs and Volmer, with modification by later workers (Shierholz, 1974). The first requirement for nucleation is a supersaturated solution. There is a critical number of molecules that must come together for new crystal formation ; if the number of molecules is greater than the critical number a crystal cluster will form and begin to grow, if the number of molecules is less the cluster will redissolve. The point where there is a critical number of molecules corresponds to a maximum on the free energy diagram. Either growing or redissolving results in a decrease in the free energy of the crystal. The free energy necessary to form a new crystal is called the critical free energy, ΔG_{crit}.

Mullin (1972) divides nucleation into two types, primary and secondary. Primary nucleation can occur by homogeneous or heterogeneous means. Secondary nucleation can occur by initial breeding, needle breeding, polycrystalline breeding or collision breeding.

Homogeneous nucleation is a spontaneous generation of nuclei which occurs at some high supersaturation level in a solution that is void of all foreign particulate matter such as dust, seed crystals, etc. This is the type of nucleation the thermodynamic theory is based on. Homogeneous nucleation occurs when a cluster of molecules has reached ΔG_{crit}. *Heterogeneous nucleation* occurs as a result of the presence of submicroscopic particles of material different from the solute. Heterogeneous nucleation occurs at lower supersaturations, thus requiring a ΔG_{crit} less than that for homogeneous nucleation. It is doubtful if homogeneous nucleation, in the strictest sense, has ever been observed, because it is virtually impossible to achieve a solution with less than 10^3 foreign bodies per cubic centimetre (Mullin, 1972). Therefore, nucleation of the primary type takes place as heterogeneous nucleation.

Secondary nucleation results from interaction between crystals or interaction between crystals and other solid objects such as the

agitator or the crystallizer wall. Strickland-Constable (1968) divides secondary nucleation into four types :

(1) *Initial breeding*, when certain types of crystals are placed into supersaturated solutions. A shower of nuclei is immediately observed which dwindles with time.

(2) *Needle breeding*, when needles or spikes called dendrites grow on the ends of crystals. These can then be broken off by fluid shear to form the new crystals. This phenomenon takes place only at high supersaturation.

(3) *Polycrystalline breeding*, when crystals are made up of small randomly oriented crystals that are broken by agitation. This also only occurs at high supersaturation.

(4) *Collision breeding*, when crystals collide with the walls of the vessel or with other crystals. Nucleation by this means occurs with extreme readiness even at very low supersaturations. This is thought to be the predominant nucleation mechanism in industrial cyrstallizers.

For a more detailed discussion on the subject of nucleation, the reader is referred to a text by Mullin (1972).

3.3 Crystal Growth - General Models

Nucleation and growth both normally occur in industrial crystallizers (Shierholz, 1974). However, if seed is present in sufficient quantities, it has been observed that below certain levels of supersaturation growth will occur but nucleation apparently will not or only to a minor extent. Also, it has been observed that even at levels of supersaturation which normally support nucleation, nucleation will not occur unless seed is introduced. Therefore, nucleation and growth can be treated as distinct phenomena.

The growth of crystals occurs in successive reaction steps, the transport of the solute to the crystal interface, the adsorption of solute at the surface and the incorporation of the crystal constituents into the lattice (Stumm and Morgan, 1970). Furthermore, the back reaction for crystal dissolution must be considered. Growth kinetics depend on the rate-limiting step. Essentially two limiting theories on growth kinetics have been established,

(1) diffusion controlled growth, and

(2) interface controlled growth.

Diffusion controlled growth may be empirically characterized by the following rate equation,

$$\frac{dC}{dt} = k.S.(C-C_o) \quad \ldots\ (2.19)$$

where C_o = equilibrium solution concentration of salt being precipitated

C = salt solution concentration at time t

k = rate constant

S = precipitate surface area

Equation (2.19) is only valid for solutions with equivalent concentrations of cations and anions of the salt being precipitated. The rate constant is a function of the salt's diffision coefficient and the level of turbulence in solution.

Interface controlled growth may be empirically characterized by the following rate equation,

$$\frac{dC}{dt} = k.S.(C-Co)^{n} \quad \ldots\ (2.20)$$

where n = order of reaction

Equation (2.20) is only valid for solutions with equivalent concentrations of cations and anions of the salt being precipitated. For interface controlled growth "n" is always greater than one. Interface controlled growth is independent of reaction solution turbulence above a critical level.

While dissolution reactions are nearly always diffusion controlled, growth of crystals frequently appears to be controlled by interfacial processes such as adsorption or dislocation steps. Equations (2.19 and 2.20) must not be accepted as definitive of a particular type of growth. Other measurements such as the effect of temperature and turbulence on the rate constant, k, will supply further evidence, either in support or rejection of the type of crystal growth intimated by Eqs.(2.19 and 2.20) (Stumm and Morgan, 1970).

Nancollas and Purdie (1964) have demonstrated that the kinetics of surface controlled crystal growth for solutions containing non equivalent concentrations of cations and anions of a salt being precipitated, may be expressed by an equation similar to Eq.(2.20), by replacing "C" by the geometric mean concentration of the cation and anion species. Consider the following general reaction,

$$xM^{y+} + yA^{x-} \longrightarrow M_xA_y \qquad \ldots\ (2.21)$$

where M = cation with charge y+
A = anion with charge x−

The rate equation for this reaction will be,

$$-\frac{dm}{dt} = k.S.\{([M^{y+}]^x[A^{x-}]^y)^{\frac{1}{x+y}} - K_{sp}^{\frac{1}{x+y}}\}^{x+y} \qquad \ldots\ (2.22)$$

where m = mass of salt precipitated

k = rate constant

S = surface area of crystals

K_{sp} = solubility product of salt $M_x A_y$

This rate equation has been shown to be valid for the precipitation of a number of salts, e.g. silver chloride, magnesium oxalate and barium sulphate, when reacting non-equivalent concentrations of reacting species, i.e. for cation to anion ratio's of 0,25 to 4,0 (Nancollas and Purdie, 1964).

The term "S" in Eq. (2.22) is the surface area term. Although it is to be expected that the rate of growth of seed crystals will be linear with respect to the surface area, there is evidence to indicate that in many systems the effective growth areas of the crystals become constant at a certain stage in the process, even though the crystals increase in size (Nancollas and Purdie, 1964). As an example, for magnesium oxalate the rate of precipitation is directly proportional to the mass of seed crystals inoculated into the supersaturated solution, and hence it appears that no additional growth sites are formed during crystallization.

Because the rate determining step is frequently controlled at the interface, small concentrations of soluble foreign constituents may alter markedly the growth rate and morphology of the precipitated crytals (Stumm and Morgan, 1970). The retarding effect of substances that become adsorbed may be explained as being primarily due to the adsorbed molecules obstructing the deposition of lattice ions. Davies and Nancollas (1955) have shown, for a number of cases, that the rate constant for crystal growth is reduced by an amount reflecting the extent of adsorption.

In addition to the description of the crystal growth process in terms of mass balances, as outlined above, energy and population balances may also be required to give a complete description of the process. Waste water precipitation processes are usually conducted isothermally

and hence energy balances are not required. However, both mass and population balances may be required. The first gives insight into the rate of crystal production, (as discussed above), whereas the second gives insight into the size and number of crystals produced.

With regard to the number of crystals formed, Shierholz (1974) reported the following fundamental relationship for calculating population balances in effluents from completely stirred tank reactor (CSTR). crystallizers,

$$n = n^{o}\exp(-L/GR) \quad \ldots\ldots \quad (2.23)$$

where n = population density of crystals with size L
n^{o} = population density of zero-size particles (the nuclei population density)
L = mean particle size
G = crystal growth rate
R = residence time

Equation (2.23) relates L and n, which characterize the Crystal Size Distribution (CSD). Hence, if an experiment is carried out at a given residence time, R , G and n^{o} can be determined from measurements of n as a function of L. Usually this is done by plotting $\ell n(n)$ versus L. The values of G and n^{o} being determined respectively from the slope of the straight line plot and its intersection with the $\ell n(n)$ coordinate at L = 0. A typical plot is shown in Appendix 18, Figure A18.5.

The kinetic information obtained from Eq (2.23) provides the design engineer of a crystallizer with answers to questions such as,

(1) how is the CSD affected by supersaturation, and

(2) how is the CSD affected by sludge recirculation.

Without this information one might make a design change thinking that this will result in an increase in crystal size whereas it may induce the opposite effect.

Randolph and Larson (1971) have reported considerable success with the following empirical model, relating nucleation rate, B^o, with degree of supersaturation in a flow-through CSTR crystallizer,

$$B^o = k_1(C-C_s)^i \quad \cdots\cdots \quad (2.24)$$

where k_1 = kinetic constant
C = species concentration
C_s = species equilibrium concentration
i = kinetic order

They further demonstrated that

$$B^o = k_N G^i \quad \cdots\cdots \quad (2.25)$$

where k_N = kinetic constant
G = crystal growth rate

and

$$n^o = k_N G^{i-1} \quad \cdots\cdots \quad (2.26)$$

By steady state operation of a CSTR crystallizer, n^o and G can be determined at a given residence time. By operating at different levels of supersaturation, or residence times, the kinetic order, i, can be obtained.

Shierholz (1974) demonstrated that it is reasonable to expect that in systems where the nucleation rate is not of the secondary type (see Section 3.2), increased suspension (sludge) density should produce larger crystals. Increased suspension density can be obtained by sludge separation and return. It is likely that the reactor residence time, $\bar{R}$, should then be replaced by the sludge age, R_s, since this parameter gives the average residence time of the suspension in the system.

As previously indicated in this section, both mass and population balances supply information on growth kinetics. Although both techniques are applicable to pure systems, population balances have limited applicability in heterogeneous systems. In lime-treated waste water at least three different inorganic salts precipitate, resulting in a sludge with a complex composite crystal size distribution. For this reason the main effort in this investigation was oriented to the study of mass balances of the various inorganic species. However, the theory outlined above possibly may be utilized with advantage for qualitative predictions regarding the effects of sludge age, reactor retention time and other parameters on the crystal size distribution, and how these parameters may be manipulated to give optimum process results. The above theory should also assist in understanding and appreciating the content of a number of publications on calcium carbonate precipitation kinetics reviewed later in this chapter.

For a detailed discussion on crystal growth the reader is referred to standard texts by Mullin (1972), Strickland-Constable (1968), Van Hook (1961) and Walton (1967).

3.4 $CaCO_3$ Precipitation Kinetics for Pure Systems

The section above dealt with precipitation as a general phenomenon. However, specific investigations into $CaCO_3$ precipitation have also been reported. These investigations were often based on hypotheses considerably at variance with those set out in the previous section. It is worthwhile therefore to review the historical development of the theory and experimentation relating to $CaCO_3$ precipitation in order to have a better understanding of why at present certain aspects are treated the way they are and also to identify more clearly the limitations of the procedures used in the past.

The first major investigation into $CaCO_3$ precipitation kinetics was reported by Stumper (1948). He studied the batch reaction of $Ca(HCO_3)_2$ with $Ca(OH)_2$ at 20°C. The reaction,

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O \quad .... \quad (2.27)$$

was followed by determining dissolved calcium concentrations in samples withdrawn from the reaction mixture at set intervals. The following general rate equation was established for solutions containing non-equivalent concentrations of $Ca(HCO_3)_2$ and $Ca(OH)_2$,

$$\frac{d[Ca^{2+}]}{dt} = k.[Ca^{2+}][HCO_3^-][OH^-] \quad .... \quad (2.28)$$

For equivalent concentrations of reactants, i.e.

$$[Ca(HCO_3)_2] = [Ca(OH)_2]$$

and hence

$$[Ca^{2+}]_T = [HCO_3^-]_T = [OH^-]_T$$

Equation (2.28) reduces to,

$$\frac{d[Ca^{2+}]}{dt} = k' \cdot [Ca^{2+}]^3 \quad \ldots\ldots (2.29)$$

Stumper also found that the introduction of seed crystals to the reaction solution "catalysed" or increased the rate of reaction very considerably, up to a hundred times or more.

The model proposed by Stumper for the precipitation kinetics of $CaCO_3$ is essentially empirical and not founded on any basic considerations such as the influence of crystal surface area, supersaturation and the dissolution back-reaction. However, a qualified basis for his model can be developed from the work of Reddy and Nancollas (1971), by making a number of simplifying assumptions (see later).

McCauley and Eliassen (1955) reported on studies of $CaCO_3$ precipitation from synthetic solutions (NaOH, $NaHCO_3$, Na_2CO_3, $CaCl_2$) in batch and continuous reactors. They chose experimental conditions which simulated $CaCO_3$ precipitation conditions in softening plants. The following observations were reported,

(1) The lime-soda softening process is a "rate process" which takes place rapidly at high concentrations of reacting substances, but proceeds slowly as the reaction approaches equilibrium.

(2) Rapid mixing with preformed crystals accelerates the reaction, indicating the value of solids-contact units.

(3) For the limited number of waters studied there is a relationship between residual calcium hardness and pH.

(4) Lime-soda removal of calcium in the presence of preformed $CaCO_3$ crystals occurs through the growth of these crystals.

(5) After recarbonation or split treatment, stirring the treated water with preformed crystals assists in producing a stable and low calcium water.

(6) Minimum calcium levels of 15 to 25 mg ℓ^{-1} (as $CaCO_3$) were obtained by stirring lime-soda softened or recarbonated waters with copious quantities of $CaCO_3$ crystals at an equilibrium pH value of about 9,8 to 10,2.

By not presenting a model for $CaCO_3$ precipitation kinetics the authors limited the general applicability of the results of their work. For example, observation (3) is limited to the specific system studied; observation (4) appears to be a limited description of the overall calcium removal process, i.e. growth of individual crystals cannot be indefinite as the crystals will eventually grow to an unmanagable size, which has not been observed. Collision breeding as proposed by Strickland-Constable (1968), in addition to crystal growth, appears a more plausible mechanism.

Reddy and Nancollas (1971) reported on the kinetics of crystallization of calcium carbonate in batch reactors from stable supersaturated solutions. The reaction was followed by monitoring changes in calcium ion concentration and pH, when adding calcite seed crystals to stable supersaturated solutions. The studies were made for slightly supersaturated solutions with pH values ranging from 8,4 to 8,8. After an initial growth surge, due to heterogeneous nucleation, the process appeared to be described by the kinetic relationship,

$$\frac{d[Ca_T^{2+}]}{dt} = k_G.S.\{[Ca^{2+}][CO_3^{2-}] - K_{sp}/f_D^2\} \quad .... \quad (2.30)$$

where $[\ _T]$ = total dissolved species concentration (mol ℓ^{-1})
$[\ ]$ = total free ion concentration (mol ℓ^{-1})
k_G = kinetic rate constant (ℓ mol^{-1} min^{-1})/(mg seed/100 mℓ)
S = crystal surface area (mg seed)/(100 mℓ)
K_{sp} = calcite solubility product (mol^2 ℓ^{-1})
f_D = activity factor for divalent ions
$\{\ \}$ supersaturation term (mol^2 ℓ^2)

By determining k_G in Eq. (2.30) at various temperatures, Reddy and Nancollas calculated the activation energy for $CaCO_3$ crystal growth to be 11,0 $\pm$ 1,0 kcal mol^{-1}. It was also shown that the reaction was independent of stirring speed. They concluded that the relatively high value for the activation energy and the independence of the reaction rate on stirring speed, indicated that the $CaCO_3$ crystallization process is surface controlled.

Reddy and Nancollas (1971) were the first to formulate $CaCO_3$ precipitation kinetics in terms of supersaturation and crystal surface area (or mass) rather than in terms of reacting species concentrations only. In this regard their work constitutes a considerable advance in knowledge on the basic behaviour of $CaCO_3$ crystallization kinetics. Criticism that can be brought against their work are,

(1) The range of concentrations of reacting substances tested is very restricted so that it is not possible to conclude that Eq.(2.30) applies in general for $CaCO_3$ precipitation. In particular, the observation that k_G in Eq. (2.30) is a constant, needs to be verified for a wider range of pH values and reactant species concentrations.

(2) Although the data appear to indicate that the reaction is surface controlled, rate Equation (2.30) conforms to the general equation (Eq. 2.19) postulated for diffusion controlled growth. Reddy and Nancollas maintain that Eq. (2.30) is of the second order and hence conforms to the requirements for surface controlled growth, but this conclusion is difficult to justify since the supersaturation term in Eq. (2.30) is raised to the power one which is indicative of diffusion controlled growth according to Eq. (2.19). Unfortunately the data reported by Nancollas and Reddy are insufficient to check if the model proposed by Nancollas and Purdie (1964) (Eq. 2.22) can be applied. In accordance with the hypothesis of Davies and Jones (1955) Eq. (2.22) is more likely to describe the surface controlled growth then Eq. (2.19). This discussion demonstrates one of the fundamental problems associated with kinetic studies, i.e. despite the effort to ascribe some basic considerations to the laws which govern the kinetics of precipitation, essentially they are empirical. In a restricted range of experimental conditions chosen for a particular study, more than one empirical model may adequately fit the experimental data. This point is illustrated by Reddy and Nancollas (1973), who fitted two different models to the same experimental data for calcium carbonate precipitation, both models fitting the data adequately. From a practical point of view, for simplicity and the least calculational effort, it is often sufficient to find the least complex model which will fit the experimental data and apply it for predictive purposes within the limited range for which the model appears to be valid.

If the rate Equation (2.30) of Reddy and Nancollas can be shown to be valid for a wide range of reacting substances, or, valid at high reacting species concentrations even though the value of k_G may change, it will still be of great practical value, particularly because it has such a simple form and relates the rate of precipitation to easily measurable parameters.

It can be noted that the rate equation for $CaCO_3$ precipitation developed by Stumper (1948), Eq. (2.28), is a simplified form of rate Equation (2.30) developed by Reddy and Nancollas (1971). This may be shown by making the following simplifying assumptions and applying them to Eq.(2.30),

(1) the dissolution rate is much slower than the precipitation rate,

$$[Ca^{2+}][CO_3^{2-}] \gg K_{sp}/f_D^{\,2} \qquad \ldots\ (2.31)$$

(2) the surface area remains approximately constant during precipitation

$$k_G.S \simeq k' \qquad \ldots\ (2.32)$$

(3) Ion-pairing effects are negligible.

Applying these three conditions to the Reddy and Nancollas rate equation, the following equation results,

$$\frac{d\,[Ca^{2+}]_T}{dt} = k'[Ca^{2+}][CO_3^{2-}] \qquad \ldots\ (2.33)$$

The carbonate ion concentration may be written in terms of the bicarbonate and hydroxide ion concentrations using the equation for the carbonate ion dissociation constant, $K_{CO_3^{2-}}$, i.e.

$$\frac{[OH^-][HCO_3^-]\ .f_M^2}{[CO_3^{2-}]\ .f_D} = K_{CO_3^{2-}} \qquad \ldots\ (2.34)$$

Substituting Eq. (2.34) in Eq. (2.33),

$$\frac{d[Ca^{2+}]_T}{dt} = k'[Ca^{2+}][OH^-].[HCO_3^-].f_m^2/(f_D K_{CO_3^{2-}}) \quad .... \quad (2.35)$$

$$= k''.[Ca^{2+}][OH^-].[HCO_3^-] \quad .... \quad (2.36)$$

which is identical to the equation derived by Stumper, i.e. Eq.(2.28) is a simplified form of Eq. (2.30). Stumper's rate equation is only valid when assumptions (1) to (3) are satisfied, i.e. high supersaturation, high surface areas and minimal reactant concentration changes. Reddy and Nancollas' rate equation does not suffer these limitations and is thus more generally applicable.

Girou and Roques (1971) made a study of the theoretical aspects related to the kinetics of calcium carbonate nucleation and crystal growth from CO_2-H_2O-$CaCO_3$ systems. The authors discussed three mechanisms for growth kinetics,

(1) kinetics controlled by diffusion,

(2) kinetics controlled by surface reations,

(3) kinetics controlled jointly by diffusion and surface reactions.

Theoretical rate equations were derived for $CaCO_3$ growth based on these three mechamisms.

Diffusion controlled growth - The rate equation proposed for this mechanism is,

$$\frac{d[Ca^{2+}]}{dt} = -K_{T_2}.\frac{S}{V}.\{[Ca^{2+}] - [Ca^{2+}]_{eq.}\} \quad .... \quad (2.37)$$

where S = surface area of the crystals
V = volume of the solution
$[Ca^{2+}]$ = concentration of dissolved calcium at time t
$[Ca^{2+}]_{eq}$ = equilibrium concentration of dissolved calcium
K_{T_2} = total transfer coefficient

Equation (2.37) is analogous to that proposed by Stumm and Morgan (1970), Eq. (2.18), if one assumes equivalent reacting ion concentrations, i.e.

$$C = [Ca^{2+}]_T = [CO_3^{2-}]_T$$

Surface Controlled Growth - The rate equation proposed for surface controlled growth, taking dissolution into consideration, is

$$\frac{d[Ca^{2+}]}{dt} = A_1 [Ca^{2+}]^2 + B_1 \quad .... \quad (2.38)$$

where $A_1 = C_1/(1 + \frac{10^{K_2-pH}}{2})$
$B_1 = C_1 . K_{sp_{CaCO_3}}$
C_1 = the rate constant
K_2 = the dissociation constant for CO_3^{2-}

Simultaneous Diffusion and Surface Controlled Growth - The rate equation proposed for the kinetics jointly controlled by diffusion and surface reactions is,

$$\frac{d[Ca^{2+}]}{dt} = K_{T_2}.\frac{S}{V}.\{[Ca^{2+}] - \frac{A_2 + (E + F[Ca^{2+}])^{\frac{1}{2}}}{2A_1}\} \quad \ldots\ldots \quad (2.39)$$

where $A_2 = K_{T_2}.S/V$

$E = A_2^2 + 4C_1^2.K_{sp}.A_1$

$F = 4A_1A_2$

The authors also presented the integrated forms of Equations (2.37, 2,38 and 2.39) and a computer programme for calculating the various "constants".

In a later paper Roques and Girou (1974) presented some of their experimental data, supporting the above models for $CaCO_3$ crystal growth. Their experimental technique consisted of placing a calcium carbonate solution of known concentration in a batch reactor and bubbling an air $-CO_2$ mixture through the solution to induce supersaturation. Only spontaneous crystallization was studied, i.e., no seed crystals were added to the batch reactor. The relationship between Ca^{2+} and time (Figure 2.2) was verified to represent four distinct stages in the crystal growth process,

(1) Region A, where the degree of supersaturation is high, ion diffusion between the solution and crystals was the limiting kinetic process,

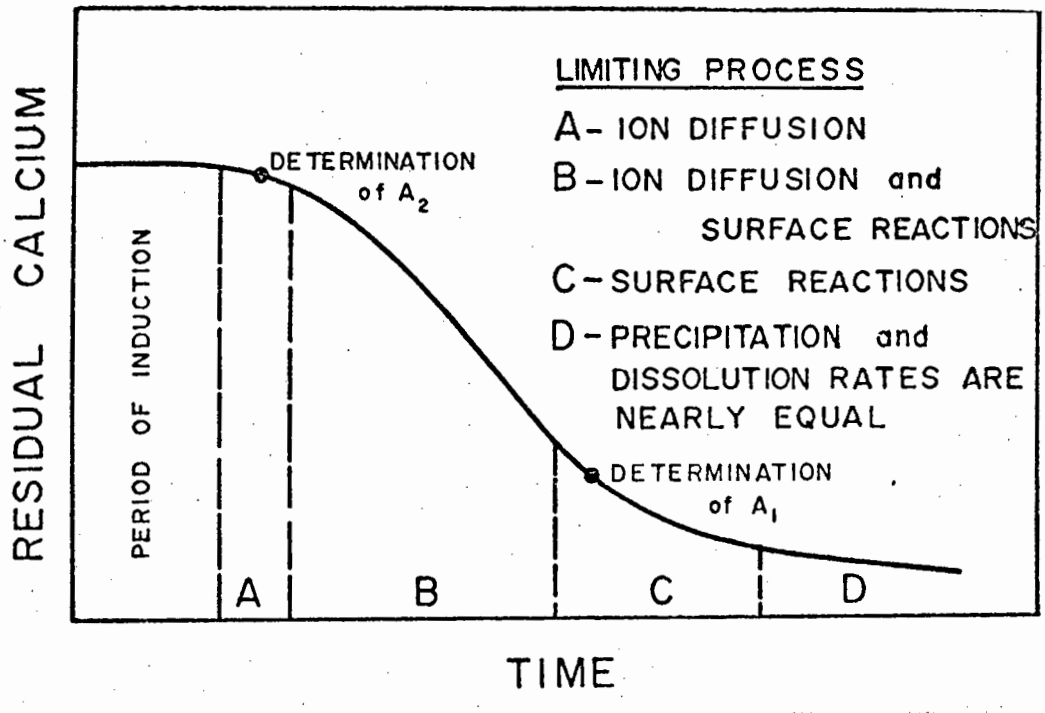

Figure 2.2. $CaCO_3$ precipitation curve indicating different regions for various rate limiting processes (After ROQUES and GIROU, 1974).

(2) Region B, the growth kinetics of crystals is controlled equally by ion diffusion and surface reactions,

(3) Region C, the rate of ion or molecular insertion in the crystalline lattice after dehydration is the limiting process, i.e. surface controlled,

(4) Region D, where the precipitation and dissolution rates are very nearly equal, i.e. approaching equilibrium.

Approximate values of A_1 and A_2 were calculated. Both "constants" are functions of pH and crystal seed area. The dispersion of the calculated A_1 and A_2 values was partially attributed to the lack of knowledge of the exact limits of regions A, B, C.

The theoretical elucidation by Girou and Roques (1971) on the mechanisms controlling $CaCO_3$ precipitation is a significant contribution to the understanding of the precipitation process, since they give a full description of this process for batch reactor systems where no crystal seed is added. The two rate equations, Eqs. (2.38 and 2.39) for diffusion and surface controlled crystal growth respectively, are not new. However, their combination for precipitation under certain specified conditions, (Region B, Figure 2.2) is an advance.

In practice $CaCO_3$ precipitation in unseeded batch reactor systems is seldom applied and hence detailed analysis of precipitation in such units is of limited practical value. In CSTR systems, which are the reactor systems most often used in practice, the growth mechanism is likely to be surface controlled, as per Eq. (2.38). The rate equation for surface controlled crystal growth proposed by Reddy and Nancollas is more explicit than Eq. (2.38). The "constants" A_1 and A_2 in Eq. (2.38) are lumped constants, i.e. a combination of two or more other constants. These are not true constants since they vary with pH and seed mass, thereby limiting the general applicability of Eq. (2.38). In contrast Reddy and Nancollas (1971) reported that their rate constant, k_G, in Eq. (2.30) is independent of pH and seed crystal concentration. They reported surface and bulk nucleation for experiments with high supersaturation and low seed mass, thereby changing the crystal population and its crystal growth properties or effectively changing the rate constant. Nevertheless, under conditions where crystal growth was predominant, their model as given by Eq. (2.30), gave a rate constant, k_G, which appears independent of pH (for narrow range studied) and seed mass.

Shierholz (1974) studied calcium carbonate crystal size distributions of precipitates formed when continuously reacting unseeded solutions of $CaSO_4$ and Na_2CO_3 in a CSTR system. It was concluded that the power law kinetic model (see Eq. 2.24) adequately described the $CaCO_3$ precipitation kinetics in this system, i.e.

(1) when $CaSO_4$ and Na_2CO_3 were reacted stoichiometrically,

$$B^o = 57\,000.G^{2,0} \quad \ldots\ (2.40)$$

where B^o = nucleation rate (numbers $m\ell^{-1}$)
G = linear crystal growth rate (microns $m\ell^{-1}$)

(2) when $CaSO_4$ was reacted with 10 percent of the stoichiometric amount of Na_2CO_3,

$$B^o = 28\,000.G^{1,7} \quad \ldots\ (2.41)$$

(3) when $CaSO_4$ and Na_2CO_3 were reacted stoichiometrically while NaOH was also added to the reaction solution to achieve Total-Phenolphthalein alkalinity ratio of 2:1,

$$B^o = 37\,000.G^{1,7} \quad \ldots\ (2.42)$$

Shierholz (1974) reported that the growth rate of $CaCO_3$ was independent of crystal size for the specific conditions studied. The predominant form of $CaCO_3$ precipitated was vaterite. It was demonstrated that the optimum condition for softening is defined by a ratio of total- to phenolphthalein alkalinity of two.

The study of Shierholz is the first literature reporting a systematic evaluation of crystal population balances for simulated lime-soda softening processes. Shierholz claims that the models (Eqs. 2.40, 2.41 and 2.42) can be used as a basis for design, i.e. as a means for choosing optimum conditions for precipitation. It is disappointing

that the author did not follow up this claim with sample calculations to demonstrate the point, or demonstrate the application to real life processes. In practice in all probability there are a large number of parameters which effect the crystal size distribution, i.e. the use of recirculated sludge, the presence of Mg^{2+} ions and trace quantities of phosphates and organic material, and therefore predictions such as those of Shierholz are likely to be of only limited value. It is also not clear what the "optimal" crystal size distribution should be. Possibly this is not critical since flocculants are often used in conjunction with the lime-soda softening process.

It is interesting to note that Shierholz (1974) reported vaterite as the predominant mineral form of the $CaCO_3$ precipitated in his CSTR system. In contrast, all the calcium carbonate sludges and scales from the Stander Plant, Pretoria, analysed as calcite with no vaterite being present. The mineral form of the precipitate may play an important role in the precipitation kinetics since the K_{sp} values for calcite and vaterite may be different (no values for vaterite could be found in the literature). Shierholz's work thus indicates the necessity to consider this aspect, specifically under the wide variety of conditions which may be encountered in practice.

The observation of Shierholz that the optimum conditions for softening is defined by,

$$\frac{\text{Total Alkalinity (T)}}{\text{Phenolphthalein Alkalinity (P)}} = 2{,}0 \qquad \ldots\ (2.43)$$

at first appears trivial, since this is inherently implied by the equation for the carbonate form of alkalinity (Standard Methods, 1975),

> "when $P = \frac{1}{2}T$ the water only contains carbonate alkalinity, i.e. carbonate alkalinity = 2P"

which has been known for a long time. However, the usefulness lies

in the sets of tables and graphs supplied by Shierholz (1974), linking the optimum pH for $CaCO_3$ precipitation with various alkalinities and temperatures. The same results, however, can be established from the Modified Caldwell-Lawrence Diagrams (Loewenthal and Marais, 1976), by noting pH and alkalinity values for solutions with zero acidity (T/P = 2) at various temperatures.

To summarize, Shierholz has reported a number of interesting and useful observations and proposed kinetic models for $CaCO_3$ precipitation. However, the direct application of his models to the lime-soda softening process is of doubtful validity and in any event not demonstrated by Shierholz.

Upto this stage all the papers reviewed relate to the precipitation kinetics of $CaCO_3$ in pure synthetic systems. Comparing the conditions under which the lime-effluent precipitation process operates with the various theoretical developments reported above, it appears that nucleation will be minimal in the presence of high precipitate (sludge) concentrations and only the kinetics of crystal growth need to be considered. Here the work of Reddy and Nancollas (1971) seems to be the most significant and further work on crystallization kinetics, either for pure systems or in application to real life processes, would probably be most fruitfully pursued by using their theory as a starting point.

3.5 $Mg(OH)_2$ Precipitation Kinetics for Pure Systems

Liu and Nancollas (1974) studied batch growth of brucite seed crystals from supersaturated solutions over a range of initial magnesium ($2{,}30 - 3{,}23 \times 10^{-4}$ M), hydroxide ($0{,}92 - 6{,}36 \times 10^{-4}$ M) and brucite crystal (34 to 170 mg ℓ^{-1}) concentrations. They employed a precision conductance method in this study to measure the progress of the reaction with time. On addition of crystals to the supersaturated solution an initial surge, followed by the subsequent slow magnesium removal from solution, was observed. The surge was attributed

to nucleation (initial breeding nucleation, see Section 3.2). The slow removal of magnesium from solution was attributed to crystal growth and recrystallization.

The results for the slow precipitation phase were modelled by the following rate equation,

$$-\frac{d[Mg^{2+}]}{dt} = k_c.S.\{([Mg^{2+}][OH^-]^2)^{1/3} - (\frac{K_{sp}}{f_1^2 f_2})^{1/3}\} \quad .... \quad (2.44)$$

where [ ] = concentration of the species enclosed within the brackets (mol ℓ^{-1})

k_c = rate constant for magnesium hydroxide crystal growth (ℓ mg^{-1} h^{-1})

S = crystal surface area available for crystal growth (mg ℓ^{-1})

K_{sp} = magnesium hydroxide thermodynamic solubility product ($mol^3 \ell^{-3}$)

f_x = activity coefficient (molar scale) of ion with charge x.

Equation (2.44) is of the same form as the general equation (2.22) for electrolyte precipitation as proposed by Nancollas and Purdie (1964), except that the supersaturation term is not raised to a power of three which would imply surface controlled growth, whereas the power of one implies diffusion control. Liu and Nancollas also presented another rate equation, which although empirical, fitted the data very well,

$$-\frac{d[Mg_T^{2+}]}{dt} = k_c'.S.\{[Mg_T^{2+}] - [Mg_{T_o}^{2+}]\} \quad .... \quad (2.45)$$

where $[Mg^{2+}_T]$ = total dissolved magnesium concentration (mol ℓ^{-1}) at time t

$[Mg^{2+}_{To}]$ = total dissolved magnesium concentration (mol ℓ^{-1}) at equilibrium

The advantage of Eq. (2.45) lies in its simplicity and hence practicality. It can be integrated quite readily, so that no sophisticated calculational techniques are needed to determine the rate constant, $k'_c.S$. It has the basic form suggested by Stumm and Morgan (1970) for diffusion controlled crystal growth (Eq. 2.19). It will be noted that the hydroxide concentration is not incorporated in this model. This is acceptable if the OH^- ion concentration, or the Mg^{2+}_T/OH^-_T ratio, is approximately constant over the range at which the experiments are conducted. Equation (2.44) does not suffer from this limitation but requires considerable computational effort to arrive at a value for $k_c.S$.

The rate equations proposed by Liu and Nancollas may serve as a basis for modelling magnesium hydroxide (brucite) precipitation in the lime treatment process. However, it is doubtful whether there are brucite crystals present in precipitated lime sludge, amorphous or semi-crystalline $Mg(OH)_2$ being more likely forms. This will affect the $Mg(OH)_2$ solubility. In the lime treatment process an additional consideration is the removal of magnesium by processes other than $Mg(OH)_2$ precipitation, i.e. magnesian calcite and magnesium silicate precipitation and Mg^{2+} adsorption onto sludge particles.

Duffau and Imbert (1974) studied magnesium hydroxide precipitation in solutions of magnesium chloride (0,02 - 0,12 M) containing seed crystals of $Mg(OH)_2$ (0-3 g ℓ^{-1}). The solutions were supersaturated by rapid addition of caustic soda. Precipitation was monitored by observing the decrease in pH as a function of time. The experimental results were modelled by the following rate equation,

$$\frac{d[Mg_T^{2+}]}{dt} = k_v.S.[Mg_T^{2+}].([OH^-] - [OH_{eq}^-])^2 \quad .... \quad (2.46)$$

Since the magnesium concentration far exceeds the hydroxide concentration for their particular experiments, Eq. (2.46) may be reduced to the following simplified form,

$$\frac{d[Mg_T^{2+}]}{dt} = k_v'.S.([OH^-] - [OH_{eq}^-])^2 \quad .... \quad (2.47)$$

which is analogous to the rate equation (Eq. 2.20) proposed by Stumm and Morgan (1970) for interface controlled crystal growth. The authors stated that they could not deduce the intrinsic mechanism of growth from Eq. (2.47), but speculated that $Mg(OH)_2$ precipitation in their experiments was in all probability a surface controlled growth phenomenon.

The application of Duffau and Imbert's model to $Mg(OH)_2$ precipitation in lime treatment will suffer from similar inadequacies as in the application of the Liu and Nancollas model (Eq. 2.45). It should be noted that the former authors worked at supersaturation values far in excess of those encountered in practice, whereas the latter authors reported results for supersaturation below those normally encountered in practice. Their rate equations differ, since one implies diffusion controlled growth by virtue of the first order rate dependence on supersaturation, whereas the other implies surface controlled growth by virtue of the second order dependence on supersaturation. A study simulating true practical conditions for a specific process will dictate which, if any, of these two models is suitable for lime-treatment design purposes.

4. EFFECT OF FOREIGN SUBSTANCES ON PRECIPITATION

4.1 Effect of Phosphates on $CaCO_3$ and $Mg(OH)_2$ Precipitation

Phosphorous containing compounds are most probably the best known and most widely utilized inhibitors for the prevention or reduction of $CaCO_3$ precipitation. They are used extensively in cooling water treatment for the prevention of scale formation in heat exchanger systems (Betz, 1971). Due to their technological and economic importance, many papers on the inhibition of scale through the action of phosphorous compounds have appeared in the literature. Sewage and sewage effluents may contain some of the following group of phosphorous compounds (Painter, 1973) : proteins, detergents and ortho-phosphates. A review follows of the major papers published on this topic which have a bearing on the work in this thesis.

Reitemeier and Buehrer (1940a) were the first to publish a comprehensive and systematic study of the effect of poly-phosphates on calcium carbonate precipitation. They studied $CaCO_3$ precipitation from solutions containing calcium bicarbonate and ammonium hydroxide. (Apparently the NH_4OH was used as a source of alkalinity). Glassy sodium hexametaphosphate, at extremely low concentrations of the order of 1 mg ℓ^{-1} (as P), was found to prevent precipitation of $CaCO_3$ from solutions containing 200 mg ℓ^{-1} calcium bicarbonate and 550 mg ℓ^{-1} ammonia (Figure 2.3). Crystalline sodium meta-phosphate was found to be relatively ineffective under similar conditions. At low calcium concentrations pyro-phosphates were found to be as effective as hexameta-phosphates. Ortho-phosphates exhibited only a slight ability to inhibit precipitation, but their effect was limited by the precipitation of calcium ortho-phosphate.

The authors also reported that the threshold concentration of hexameta-phosphate to prevent precipitation increased with ammonia and calcium bicarbonate concentrations; at lower concentrations hexameta-phosphate retards precipitation and only if present in sufficient concentrations will it prevent precipitation entirely.

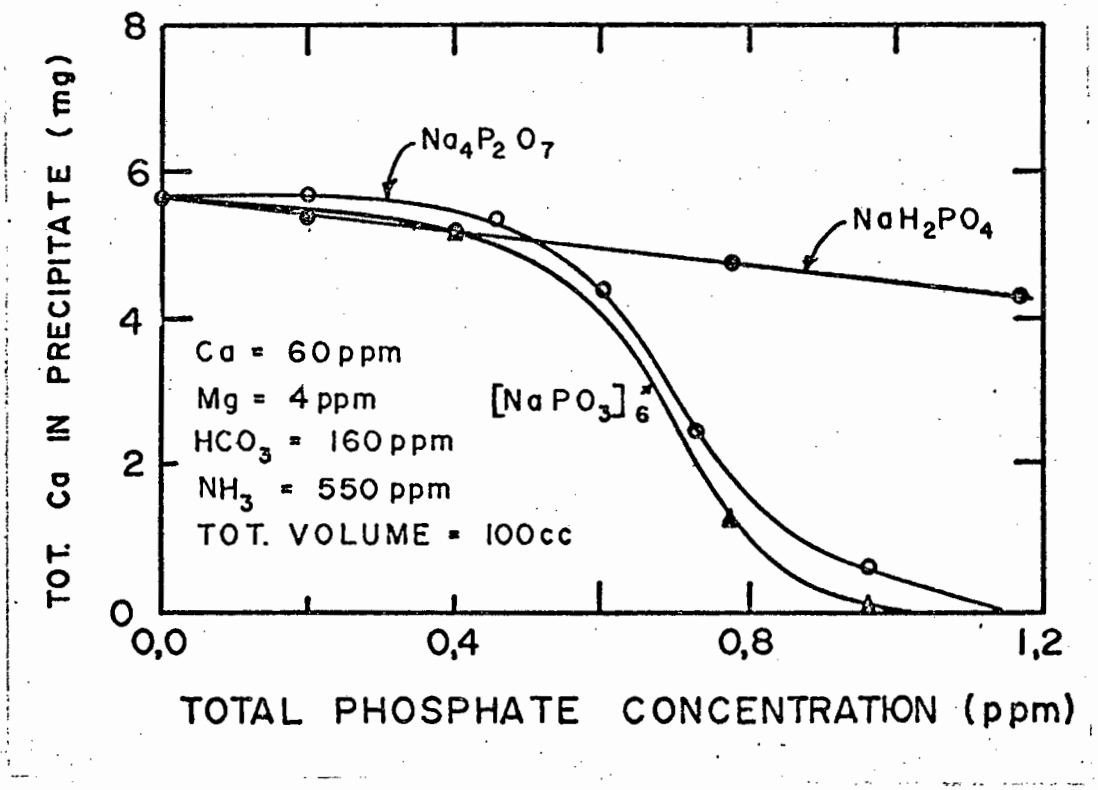

Figure 2.3. Inhibiting action of various phosphates on $CaCO_3$ precipitation (After REITEMEIER and BUEHRER, 1940a)

In a second paper Buehrer and Reitemeier (1940b) reported that hexameta-phosphate forces the crystallization of larger, fewer, and grossly distorted crystals in the place of the typical rhombs of calcite. Meta-, pyro- and ortho-phosphates possess in varying degrees this ability to hinder the process of crystallization. X-ray powder spectrograms showed that the distorted crystals obtained in the presence of these phosphates are true calcite, although their exterior surfaces may show complete absence of typical polyhedral faces. Chemical studies of the precipitates indicated that the meta-phosphate is adsorbed by the calcium carbonate in amounts such that the Ca/P mass ratio attains a constant value of approximately 300 in the presence of meta-phosphate concentrations greater than 0,6 mg ℓ^{-1}, the concentration at which adsorption reaches a maximum. The mechanism of the inhibition process is postulated to involve primarily restricted or deranged crystallization due to the adsorption of the meta-phosphate

on the crystal faces.

The work of Reitemeier and Buerer gives a general impression of the effects of various simple and poly-phosphates on calcite precipitation, i.e. crystal distortion, retardation and even complete inhibition of precipitation. They proposed an adsorption mechanism to account for these observations. However, the systems they studied are very dissimilar to the lime-secondary effluent system. Specifically in secondary effluent, the major phosphorous component will be ortho-phosphate (± 90 percent) with minor components (± 10 percent) being proteins (or various break down products), detergents and organo-phosphorous compounds, rather than poly-phosphates. In the lime treatment of secondary sewage effluents ortho-phosphate is essentially completely removed at pH values in excess of 10,0. The question thus remains whether the ortho-phosphate completely precipitates as say tricalcium phosphate or still exerts some inhibiting properties during precipitation. The second question which remains unanswered is whether the organo-phosphates, which are only partially (0-30 percent) removed by lime treatment, exert any inhibiting effects.

Reddy and Nancollas (1973) studied the growth kinetics of calcium carbonate in the presence of several phosphonic acid derivatives. Growth was studied by monitoring pH and dissolved calcium with time in supersaturated calcium carbonate solutions ($CaCl_2$, $NaHCO_3$, NaOH) which were inocculated with preformed calcite crystals. The rate equation describing the removal of calcium from solution is given as,

$$- \frac{d[Ca^{2+}]}{dt} = k.S.([Ca^{2+}] - [Ca^{2+}_{\infty}])^2 \quad \ldots\ldots \quad (2.48)$$

The authors do not explain why they did not use the more comprehensive model for $CaCO_3$ precipitation, i.e. Eq. (2.30), which they proposed in a previous paper. It would appear however that Eq. (2.48) is used for its simplicity and hence ease of calculation. This equation is an acceptable simplification only if the carbonate concentration greatly exceeds the calcium concentration, which was the case in their experiments - typical carbonate and calcium concentrations were $1{,}00 \times 10^{-2}$ M and $11{,}70 \times 10^{-5}$ M, respectively.

The value of the rate constant, k, was significantly effected by the presence of phosphonic acid derivatives; it was reduced by 62 to 99 percent in the presence of 0,08 to 2,5 mg ℓ^{-1} derivative respectively. The authors reported that a Langmuir isotherm,

$$\frac{k_o}{k_o - k} = \frac{1 + k_2}{k_1 C} \qquad \ldots\ (2.49)$$

where k_o = crystal growth rate in absence of derivative
k = crystal growth rate in presence of derivative
k_1 = rate constant for desorption of derivative
k_2 = rate constant for adsorption of derivative
C = concentration of derivative

satisfactorily describes the inhibiting effects of the phosphonic acid derivatives (see Figure 2.4). On the basis of this model they explained the inhibition mechanisms in terms of a mono molecular layer of foreign ions blocking growth sites on the crystal surfaces. Although the authors plotted a straight line through their experimental data this is not substantiated by the plot in Figure 2.4.
This does not summarily exclude the adsorption mechanism, for the Langmuir isotherm may not adequately model the data. Consideration of other adsorption models could result in improved fits.

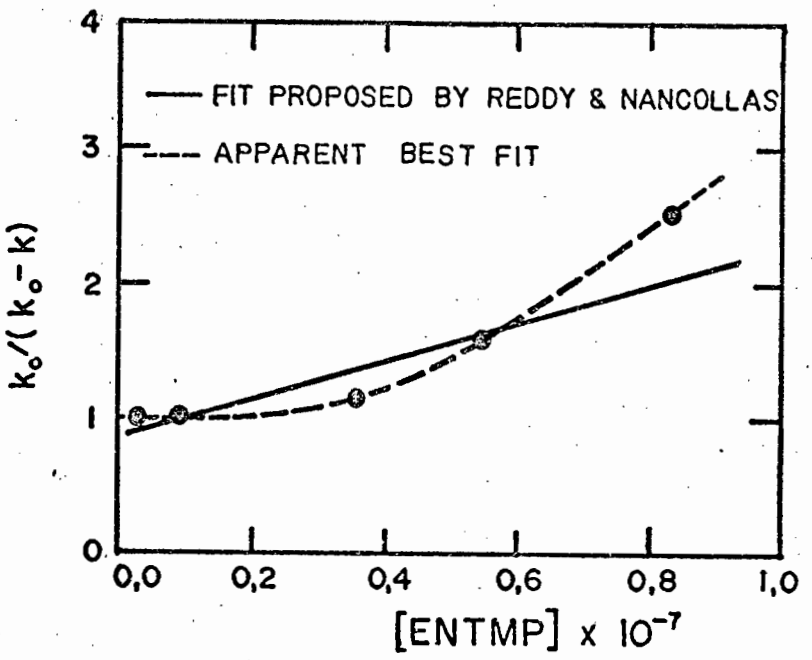

Figure 2.4. Langmuir isotherm plot for the $CaCO_3$-ENTMP system (After REDDY and NANCOLLAS, 1973)

Reddy and Nancollas were the first to present a rate equation modelling the retarding effect phosphorous containing compounds have on calcium carbonate precipitation. They were also the first to provide evidence for the adsorption isotherm. Unfortunately the work cannot be applied directly to lime-treated sewage effluents since these effluents do not (as a rule) contain phosphonic acid derivatives. However, Eqs. (2.48 and 2.49) may serve as a basis for establishing the effects of other organo-phosphates and ortho-phosphate on $CaCO_3$ precipitation in the lime treatment process.

Griffin and Jurinak (1973) studied the adsorption of ortho-phosphate on calcite crystals. Their studies were conducted by shaking aqueous suspensions of 4,0g of $CaCO_3$ placed in 50 mls of stock K_2HPO_4 solutions. The initial P concentrations ranged from 0,1 to 5,0 mg ℓ^{-1}. The adsorption isotherms of phosphate on calcite were

shown to be described by a two-region Langmuir isotherm equation,

$$\frac{C}{x/m} = \frac{1}{K.B} + \frac{C}{b} \quad \ldots\ (2.50)$$

where C = equilibrium concentrations of the phosphate
x/m = amount of phosphate adsorbed per unit mass of adsorbent
b = phosphate adsorption maximum
K.B = a term related to the energy of adsorption

On a solubility diagram for calcium phosphates (Figure 2.5), the break in the slope of the Langmuir plot corresponded closely to the division between octo-calcium phosphate and hydroxy apatite. In explaining this phenomenon the authors concluded that adsorption and heterogeneous nucleation (of the two above-mentioned phosphates) are inseparable when describing the interaction of ortho-phosphate with calcite. The work thus verified the speculation by Buehrer and Reitemeier, i.e. ortho-phosphate does adsorb onto calcite. Griffin and Jurinak's work covers ortho-phosphate adsorption onto preformed calcite at a pH of 8,4. No evidence was presented as to whether this adsorption results in the inhibition of calcium carbonate precipitation.

Capri and Marais (1975) conducted a series of precipitation experiments to determine the inhibitory effect of different ortho-phosphate concentrations on $CaCO_3$ precipitation. The experiments were conducted to determine the effect of $Ca(OH)_2$ addition on the pH in anaerobic digestion. The experiments were performed on deionized water and anaerobic process liquor. Deionized water samples were prepared with ortho-phosphate (Na_2HPO_4) concentrations of $0{,}1 \times 10^{-3}$, $0{,}5 \times 10^{-3}$, $1{,}0 \times 10^{-3}$ and $6{,}0 \times 10^{-3}$ mol ℓ^{-1} at 20°C. A stream of

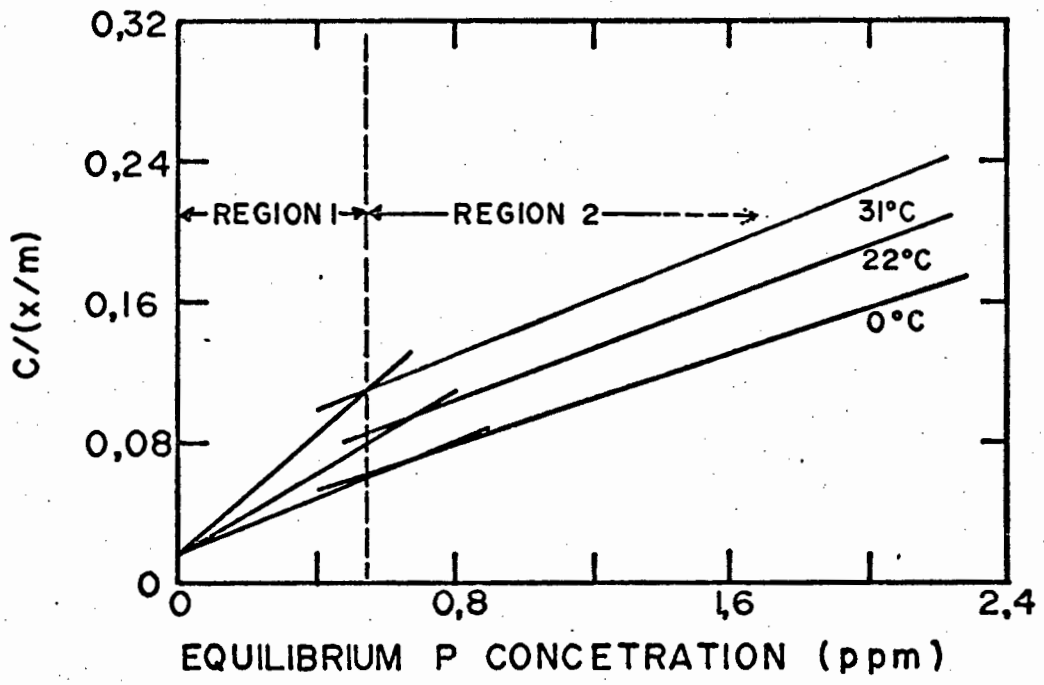

Figure 2.5. Phosphate adsorption data for calcite plotted according to the Langmuir isotherm (After GRIFFIN and JURINAK, 1973)

39 percent CO_2 was bubbled continuously through the liquid. Initial pH values were adjusted to 6,0 - 6,4 by addition of H_2SO_4. Lime was incrementally fed and the pH taken after each addition once equilibrium was attained ($\pm$ 10 min.). With each lime addition the pH increased and some precipitation took place.

In samples containing no phosphates the pH remained constant at the value where the calcium carbonate activity product value was equivalent to the K_{sp} for calcite. However, with phosphate present only 55 percent of the $Ca(OH)_2$ (as $CaCO_3$) was precipitated, i.e. inhibition kept the remaining 45 percent in solution. This behaviour continued until a calcium concentration approximately fifty times the concentration of phosphate was in solution, when the phosphate itself precipitated from solution. Thereafter the behaviour reverted to that in samples containing no phosphate. The pH measurements showed that Ca^{2+} and CO_3^{2-} ions

had not reacted to completion, since their activity products exceeded the value for the calcite solubility product. However, tests in which the solutions were left for 24 hours did not show any further precipitation. It was concluded that ortho-phosphate in some way directly affected the solubility of calcite.

The work of Capri and Marais illustrates the critical role which ortho-phosphate may play in lime-treated secondary effluent. The pH range studied by these authors is considerably lower than that normally found in the high lime treatment, i.e. 6,0 - 7,5 as opposed to 11,0 - 11,5. Therefore, their work does not indicate if phosphates left after high lime treatment may significantly affect the final stable concentration of Ca^{2+} in the treated water.

Liu and Nancollas (1973) studied the effects of various phosphonic acid derivatives on magnesium hydroxide crystal growth. (For experimental details see Section 3.5). The rate constant, k_c, in Eq. (2.44) was found to be reduced by the presence of the phosphonate derivatives. However, the inhibiting effect on $Mg(OH)_2$ crystallization was much less than that in the case of calcium carbonate or calcium sulphate crystallization.

Although this work does not directly relate to the lime-treated secondary effluent system, since phosphonates are not generally expected in this system, it is interesting to note that magnesium hydroxide crystal growth was effected only to a minor extent by phosphorous compounds.

4.2 Effect of Mg^{2+} on $CaCO_3$ Precipitation

Sewage effluent hardness is usually due to both calcium and magnesium ions. In Pretoria Sewage Works secondary effluent the calcium and magnesium hardness are both of the order of 50 to 100 mg ℓ^{-1} (as $CaCO_3$). In the High Lime Process a major fraction of the magnesium hardness is removed by precipitation as magnesium hydroxide. A question which thus arises is whether the Mg^{2+} ions remaining in solution, and possibly those co-precipitated during the lime treatment, have any sig-

nificant effect on the rate of precipitation and solubility of $CaCO_3$. A review of some of the major papers published on this topic is given below.

Brooks, Clark and Thurston (1951) studied the formation of the various forms of $CaCO_3$ which exist in the $CaCO_3$-H_2O system, by manipulation of experimental conditions and addition of substances such as magnesium salts. Calcium carbonate was precipitated by slowly dripping solutions containing magnesium chloride (60 mℓ, 12 percent), calcium chloride (126 mℓ, 25 percent) and sodium carbonate (91 mℓ, 25 percent) into a well stirred solution of saturated sodium chloride (400 mℓ) at temperatures ranging between -10 and 10°C. The various forms of calcium carbonate which precipitated were : $CaCO_3.6H_2O$ at -10°C, $CaCO_3.H_2O$ at -2°C and calcite at 10°C. Chemical analysis of the precipitates indicated that appreciable quantities of magnesium had been incorporated into, or adsorbed onto the calcium carbonate precipitates. The authors concluded that the presence of magnesium ions during calcium carbonate precipitation results in the distortion of the calcite phase, inhibition of calcite precipitation and spontaneous precipitation of other phases such as calcium carbonate mono- and hexa-hydrate.

Kitano (1962) studied the influence of Mg^{2+} on the crystallization of calcium carbonate. Different quantities (0-6g) of magnesium salts ($MgCl_2$, $MgSO_4$, $Mg(HCO_3)_2$) were placed in glass flasks with distilled water and a saturated calcium bicarbonate solution. The flasks were left to stand at room temperature for two to three weeks, during which time carbon dioxide gas escaped from the solution and calcium carbonate crystals precipitated. The precipitates were chemically analysed and the various crystal forms were identified by X-ray diffraction techniques. Kitano found that high concentrations of magnesium ions favoured aragonite formation very strongly. The presence of magnesium chloride was more favourable to aragonite formation than magnesium bicarbonate or magnesium sulphate. At low Mg^{2+} concentrations only calcite precipitated. Magnesium was not coprecipitated with calcium carbonate (calcite). It is of interest

to note that no magnesium was removed from solution during precipitation. This may possibly be related to the slow precipitation (2 to 3 weeks) and the low pH range (6,7 - 8,1), i.e. no Mg^{2+} was entrapped in the precipitates and the pH was too low for $Mg(OH)_2$ to precipitate. Since no magnesium was removed from solution, this implies that the inhibition mechanism must be one of the prevention of calcite nuclei formation rather than adsorption of Mg^{2+} onto precipitates. Another possible explanation is that magnesium ions were entrapped in the precipitated $CaCO_3$, but were removed from the $CaCO_3$ matrix through the establishment of solid-solid equilibrium over the relatively long reaction period allowed in these experiments.

Möller and Rajagopalan (1975) studied the precipitation kinetics of $CaCO_3$ in the presence of Mg^{2+} ions. Their main interest was to study $CaCO_3$ nucleation under conditions which could be related to natural environments. They used the technique of precipitation from homogeneous solutions, i.e. no seed crystals were added. Saturated solutions of calcium carbonate were mixed with solutions containing magnesium chloride and radio-active calcium (Ca-45). Air was bubbled through these solutions resulting in CO_2 removal with subsequent calcium carbonate precipitation. The precipitation was monitored by counting β-particles from Ca-45 decay. The authors found that for any given degree of precipitation and up to a Mg/Ca molar ratio of about 4, the rate of precipitation and the rate of nucleation were higher for calcite or magnesian calcite than for aragonite, the latter only precipitating at higher Mg/Ca molar ratios. The following rate equation was found to model adequately the precipitation results,

$$\frac{dC}{dt} = k_p.(C-S)^P \qquad \ldots. \quad (2.51)$$

where k_p = growth rate coefficient
p = order of growth process
C = calcium carbonate concentration
S = saturation calcium carbonate concentration

The value of the growth order, p, remained constant at 4 in the Mg/Ca molar ratio range of 0 to 6,6 indicating that the rate controlling reaction did not change over this wide range of molar ratios. It would appear that the rate of growth was also little affected by the wide range of molar ratios.

Black and Christman (1961) reported electrophoretic studies on sludge particles produced during simulated lime-soda softening process experiments. They reacted solutions containing $CaCl_2$, $NaHCO_3$, $MgCl_2$, $Ca(OH)_2$ and NaOH, in a standard jar test machine. Electrophoretic mobilities of the particles of $CaCO_3$ and $Mg(OH)_2$ were measured. The zeta potential of $Mg(OH)_2$ was found to be positive throughout the entire pH range encountered (9,0 - 11,0) in lime-soda softening. The zeta potential of the $CaCO_3$ particles was found to be negative in the absence of Mg^{2+}, but the potential became less negative and finally became positive as the ratio of magnesium to calcium in the water being softened was increased. This charge reversal was attributed, at least in part to Mg^{2+} adsorption on calcite. Up to 10 percent of the magnesium hardness was reported to be removed by this mechanism.

Black and Christman (1961) were the first to make a systematic study of $CaCO_3$ precipitation in the presence of Mg^{2+} ions under simulated lime-soda softening conditions. They demonstrated that a significant amount of magnesium was removed from solution by a process(es) other than precipitation. The diminishing and eventual reversal of the charge on the negatively charged calcite particles suggested Mg^{2+} adsorption onto the calcite surface. They did not investigate aspects relating to the solubility of the calcite formed in the lime-soda softening process and the rate of $CaCO_3$ precipitation.

Chave, Deffeyes, Weyl, Garrels and Thompson (1962) investigated the solubility of magnesian calcites at 25°C and one atmosphere pressure. They found that as the Mg/Ca ratio in the magnesian calcites increased, so the magnesian calcite solubility increased. Using their results Winland (1969) calculated the solubility product for each of a series of different magnesian calcites. For mole fractions of Mg^{2+} in

$CaCO_3$ crystals ranging from about 0,002 to 0,15, the pK_{sp} value decreased from 8,3 to 7,8, which is equivalent to a solubility increase of about two.

Winland (1969) measured the distribution of Mg in the magnesian calcite crystals with respect to the Mg_T^{2+}/Ca_T^{2+} ratio in bulk solution surrounding the crystal. The molar fraction of Mg in the crystal, x, is given by,

$$x = \frac{1}{1 + \frac{[Ca]_s}{[Mg]_s}} \quad .... \quad (2.52)$$

where $[Ca]_s$ = calcium concentration in crystal (mol ℓ^{-1})
$[Mg]_s$ = magnesium concentration in crystal (mol ℓ^{-1})

The value of x may also be calculated from bulk solution concentrations of Mg_T^{2+} and Ca_T^{2+}, i.e.

$$x = \frac{1}{1 + \frac{[Ca^{2+}]}{0,02[Mg^{2+}]}} \quad .... \quad (2.53)$$

where Ca_T^{2+} = dissolved calcium concentration (mol ℓ^{-1})
Mg_T^{2+} = dissolved magnesium concentration (mol ℓ^{-1})

Knowing x, the pK_{sp} for a specific magnesian calcite, pK_{spm}, may be calculated, i.e.

$$pK_{spm} = 8,0 - 1,77x \quad .... \quad (2.54)$$

Although many waters do not have Mg_T^{2+}/Ca_T^{2+} ratios exceeding one, this may change when softening such waters, i.e. a major portion of the calcium hardness will be removed while only little magnesium is removed during lime-soda softening at pH 10. The nett effect will be that the Mg/Ca ratio in the bulk solution increases. The final Mg/Ca ratio may be as high as 10, with a correspondingly high magnesian calcite solubility.

The effect of magnesium then is to result in apparent incomplete $CaCO_3$ precipitation. It may be expected if magnesian calcite forms, that the rate of apparent calcite precipitation will be reduced. Berner (1975) in fact has reported that Mg^{2+} reduces the rate of $CaCO_3$ precipitation.

4.3 Effect of Organic Matter on $CaCO_3$ Precipitation

Effluents from sewage treatment processes all contain dissolved organic matter. Measured as COD, values of 20 to 50 mg ℓ^{-1} are not uncommon. The composition of this organic matter is not accurately known, but various functional groups which could be present have been reported by Painter (1973), i.e. carbohydrates, amino acids, volatile acids, non-volatile acids, neutral volatile compounds, steroids, tannins and lignins, anionic detergents, non-ionic detergents, optical brighteners, organo-chlorine compounds, polysaccharides and proteins. A few studies have been reported on the effect of individual organic compounds on calcium carbonate precipitation. The major findings of one of these studies are given below.

Kitano and Hood (1965) found that the compounds : citrate, maleate pyruvate, glycylglycine and glycogen greatly reduce the rate of calcium carbonate precipitation and favour formation of calcite. Other compounds affect the rate of formation to a moderate degree and have mixed effects on the final crystal form. Glutamate causes vaterite and calcite to precipitate; lactate, chondriotinsulphate, succinate and arginine favour calcite formation; glycine and serine favour vaterite and aragonite precipitation; and taurine causes aragonite to precipitate. The compounds galactose, dextrose, alanine and acetate have little effect on the rate of formation and do not influence the forms precipitated.

The study of Kitano and Hood demonstrates the variety of effects various organic substances may have on $CaCO_3$ precipitation. However, it is clear that this type of study, i.e. a study of the effects of individual organic substances, does not suffice for predictive purposes for the lime-treated secondary effluent system. As Painter indicated, sewage effluent contains a wide variety of organic compounds, and hence to study the effect of any one in isolation is unrealistic. The only practical approach appears to be to study the combined effect of all organic matter on $CaCO_3$ and $Mg(OH)_2$ precipitation in a specific effluent under consideration.

5. LIME TREATMENT

5.1 Lime-Treated Surface and Groundwater*

The main objective of lime-treating groundwater is usually to soften it, i.e. to remove calcium and magnesium hardness by precipitation as $CaCO_3$ and $Mg(OH)_2$. The theoretical lime, soda ash and carbon dioxide requirements for softening can be readily predicted from Modified Caldwell-Lawrence Diagrams (Loewenthal and Marais, 1976), if the pH, total alkalinity, calcium and magnesium concentrations of the raw water are known. For water free of phosphorous containing substances, the Diagram is probably the most powerful method available to assess the chemical treatment dosages required to obtain a specified or desired treated water quality. This solution is based on equilibrium chemistry and hence gives no information on the kinetics of the softening reactions or the characteristics of the precipitated sludge - in practice the turbidity and filterability of the softened water may critically influence the crystal shape and size.

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*not effluents

Hartung (1972) expressed the opinion that the best understanding of softening characteristics of a water is to be gained from the experimental softening of water with varying amounts of lime, using the standard jar-test procedure. A plot of residual calcium, magnesium and total alkalinity after the water has been treated with various amounts of lime, is a graphic description of the softening characteristics of that water. This procedure may have been necessary prior to the development of the Diagram, but certainly a large measure of this information can now be obtained from such a Diagram. Furthermore, batch tests can be misleading, since conditions reigning in them do not necessarily pertain to CSTR systems. Consider the addition of lime to result in lime softening at a pH of 10,0. At the moment that a shot-dose of lime is added to the batch reactor the pH may rise to say 11,0 and subsequently reduce to 10,5 in say 1 to 2 minutes. This may result in magnesium hydroxide precipitation during the high pH period. In a continuous process, however, the pH remains at a steady state value determined by the rate of addition of lime, and $Mg(OH)_2$ will not precipitate. The predictions from the Diagram give equilibrium values, and hence results closer to completely stirred tank reactor (CSTR) systems (i.e. widely applied practical systems) than batch tests (i.e. laboratory systems). Of course it is possible to add the lime slowly in a batch test, to create conditions closer to the CSTR system.

Hartung (1972) reported the softening characteristics for two well waters determined by the jar-test method. The differences in the softening characteristics of the two well waters are explained in terms of their different concentrations of calcium, magnesium and total alkalinity. Hartung pointed out that the mass of hardness precipitated per unit of lime added to the raw water can be increased by mixing the raw water and lime with previously precipitated hardness. These solids act as seed or crystal surfaces upon which precipitation can take place. Seeding of lime-treated natural waters also resulted in the reduction of calcium carbonate supersaturation, often found for

these effluents. The reported laboratory studies showed that with lime softening in the presence of about 5 percent or more (by mass) of previously precipitated slurry and a mixing contact time of about 30 minutes, residual calcium hardness in the treated water can be reduced to near calcite solubility values.

The experimental technique for determining a specific water's softening characteristics, as suggested by Hartung, adds a practical dimension to the theoretical predictions based on Modified Caldwell-Lawrence Diagrams. However, as stated before, CSTR system studies will give more realistic results than batch tests. The best data for design purposes will be obtained from pilot scale tests on the actual water to be treated.

Bhattacharyya, Sarkar and Dutta (1965) reported the effects of very low concentrations of ortho-phosphate (0-5 mg ℓ^{-1} as PO_4) on cold lime softening of surface waters in laboratory jar-test experiments. They found that ortho-phosphate inhibits the precipitation of calcium carbonate and keeps it in solution much above its normal solubility limit, i.e. by as much as 15-47 mg ℓ^{-1} (as $CaCO_3$). They found the inhibiting effect to be a function of the residual phosphate level of the treated waters rather than the initial amount of phosphate. Recycled sludge assisted in the removal of the phosphate interference to a limited degree, but even at a sludge concentration of 5000 mg ℓ^{-1} the interference remained significant. Coagulative removal of phosphates was applied to reduce the phosphate interference. The coagulants studied arranged in order of efficiency were : sodium aluminate>alum>ferrous sulphate>ferric sulphate.

The results reported by Bhattacharyya *et al* are consistant with observations by Capri and Marais (1975), i.e. ortho-phosphate inhibits calcium carbonate precipitation. The observation, that by means of sludge recirculation and addition of coagulants the inhibition can be partially removed, is of significant practical value.

5.2 Lime-Treated Waste Water - Laboratory and Pilot Plant Studies

Many studies on the lime treatment of waste water have been published. For a general review on this topic the reader is referred to a paper by Bernhoff (1974). Unfortunately, most of these papers do not deal in any depth with the precipitation aspects of the lime treatment process. Papers dealing more specifically with the precipitation aspects are reviewed below.

Stamberg, Bishop, Warner and Griggs (1971) reported on batch laboratory lime precipitation experiments of municipal waste water. They studied a variety of waste waters and synthetic solutions, raw waste water, secondary effluent, nitrified effluent, extended aeration effluent, organic-free synthetic solutions and secondary effluents with added ions. The effect of various lime additions on each effluent was tested using the standard jar test with flash mixing for one minute at 100 rpm, flocculation for 15 minutes at 30 rpm and 30 minutes settling.

The authors presented plots of residual calcium and magnesium concentrations versus pH for all the lime-treated effluents mentioned above (see Figure 2.6). These plots clearly indicate the different softening characteristics of the various effluents. The authors noted that with respect to total phosphate and organic materials, the lower the concentration of these, the more complete was the $CaCO_3$ precipitation. The effluents were classified as follows, in decreasing quality : nitrified effluents<secondary effluents<raw waste water. Partial $CaCO_3$ precipitation inhibition is indicated by comparing the residual calcium versus pH curves for the various effluents with the residual curve predicted from a Modified Caldwell-Lawrence Diagram with a pK_{CaCO_3} value of 8,3. The comparison indicates that $CaCO_3$ precipitation is partially inhibited in the pH range 8,0 to about 11,4. Stamberg *et al* did not investigate whether the inhibition was permanent, i.e. if longer reaction times would have resulted in more complete $CaCO_3$ precipitation. Neither did they investigate any additional means to overcome this inhibition, for example sludge recirculation.

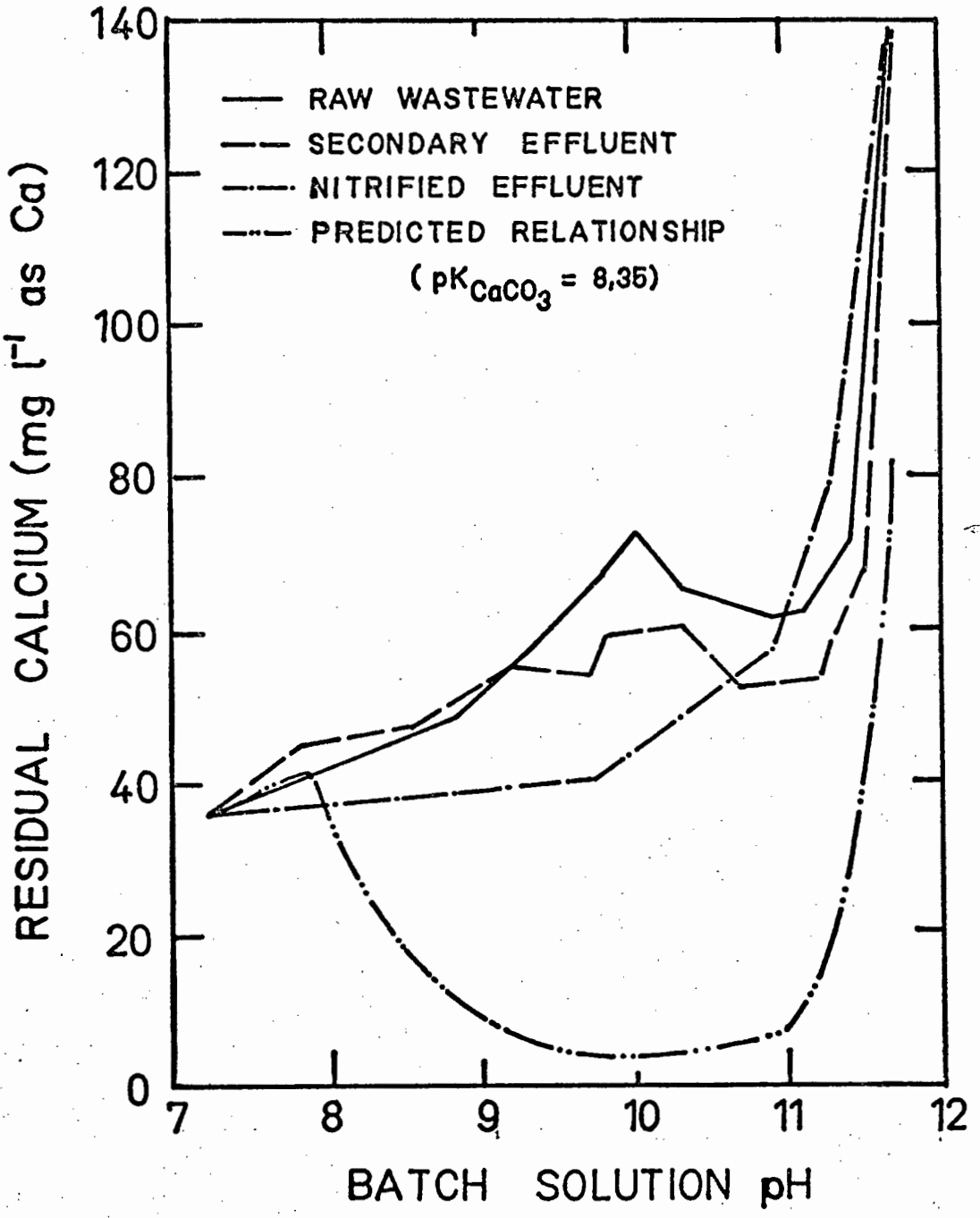

Figure 2.6. Inhibition of calcium carbonate precipitation in lime-treated waste water (After STAMBERG, BISHOP, WARNER and GRIGGS, 1971)

Berg, Brunner and Williams (1970) reported on pilot plant ($17 m^3 h^{-1}$) single stage lime clarification of secondary effluent. Their pilot plant consisted of a single stage upflow clarifier, two dual-media filters, storage tanks for backwash water and sludge, and sludge drying beds. The clarifier consisted of three distinct zones,

(1) A primary reaction zone where rapid mixing of secondary effluent, lime slurry, and sludge took place. Internal sludge recirculation was accomplished by the positive action of an impeller which drew sludge from the clarifier bottom.

(2) A secondary reaction zone which directed the flow downward through the sludge blanket while the chemical reactions took place.

(3) A sedimentation zone where the solids settled out.

Lime addition was varied to affect effluent pH values in the range 9,0 to 11,0.

Figures 2.7 and 2.8 illustrate residual calcium and magnesium as a function of pH in the filter effluent. From this data several observations may be made,

(1) There is a significant scatter of data for residual calcium and magnesium for any specific pH. In contrast to jar test results which usually give a fairly smooth residual Ca_T^{2+} and Mg_T^{2+} versus pH relationships, the results from this continuous process demonstrate the variability in such processes. Reasons for this variability may be due to variations in : raw water quality, reaction time (due to raw water flow fluctuations), sludge concentration (due to withdrawal rates not being equivalent to production rates) and temperature (seasonal fluctuations).

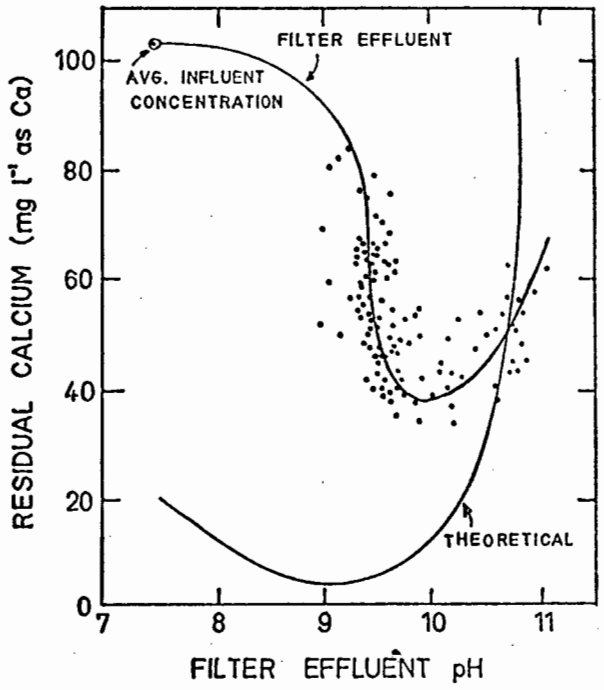

Figure 2.7. Experimental and theoretical concentrations of calcium as a function of pH for lime-treated secondary effluent (After BERG *et al*, 1970)

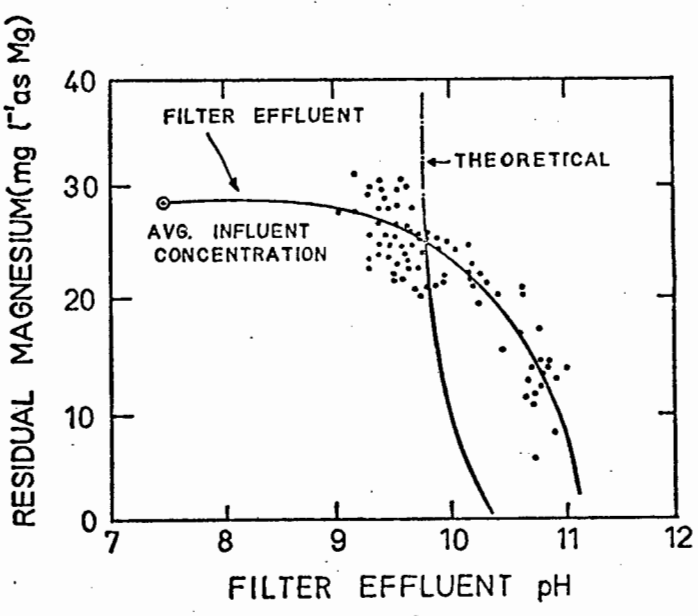

Figure 2.8. Experimental and theoretical concentrations of magnesium as a function of pH for lime-treated secondary effluent (After BERG *et al*, 1970)

(2) The calcium and magnesium residuals are not in good agreement with those predicted from calcite and brucite solubility products. The authors attributed these discrepancies to retarded precipitation and crystal distortion. Unfortunately the authors did not established if calcite and brucite were the crystallographic forms actually precipitated in their particular application of the lime treatment process.

Berg *et al* (1970) observed that the effluent from their pilot clarifier was unstable, since pipes and filter media suffered from incrustation problems. They found by lowering the effluent pH to 8,8 with sulphuric acid that the incrustation problem was eliminated. At a pH of 8,8 the Langelier Saturation Index (LSI) for this particular water is +1,0 which, theoretically, should result in scale formation. It may thus be concluded that $CaCO_3$ has a considerably higher solubility in lime-treated secondary effluent than predicted for calcite. These results are consistant with similar observations for two stage recarbonated effluents reported by Culp and Culp (1971).

Merrill (1974) made a detailed study of primary effluent lime treatment as reported in his Ph D thesis:"High Rate Treatment of Raw Domestic Sewage by Lime Precipitation and Dissolved Air Flotation." A number of the more important findings of this work have been published in papers by Mennell, Merrill and Jorden (1974), Merrill and Jorden (1974) and Merrill and Jorden (1975). The experimental studies centred around a continuous bench-scale pilot plant, comprising a feed holding tank, split feed tank, rapid mix tank, flocculation tanks, and a flotation column. The plant was designed to treat up to 60 $\ell\ h^{-1}$ primary effluent. A feature of this system was its flexibility, the design allowing for variations in rapid mixing and flocculation conditions independent of the flotation step.

The authors investigated solid (slurry) versus liquid (saturated solution) lime addition to primary effluent in relation to system performance. They found consistently lower ortho-phosphate residuals during operation with dissolved lime ($CaCl_2$ + NaOH) as compared to operation with lime slurries ($Ca(OH)_2$). They concluded that the lime slurry was not completely dissolved and hence only partially used. Since the use of $CaCl_2$ and NaOH is uneconomical, methods were studied to improve lime dissolution.

The first method investigated was to increase the intensity of rapid mixing of lime slurry with effluent. Mixing intensities were varied from average velocity gradients, $\bar{G}$, of 120 to 3 860 sec^{-1}. The results, in terms of total phosphate removal and improved effluent turbidity (Figure 2.9) indicated that for a direct lime slurry feed, average velocity gradients in the order of 2 300 sec^{-1} were required for efficient lime utilization. However, Merrill (1974) subsequently showed that applying a $\bar{G}$ value of approximately 2 300 sec^{-1} would result in prohibitive electrical costs. Re-investigation of this problem suggested that a $\bar{G}$ = 624 sec^{-1}, corresponding to a power requirement of 7hp/MGD (≈1,4 W/m^2/d) in a reactor of 5 minutes nominal detention time, gave satisfactory results for phosphate precipitation. The authors did not specify whether these conditions resulted in essentially complete lime dissolution.

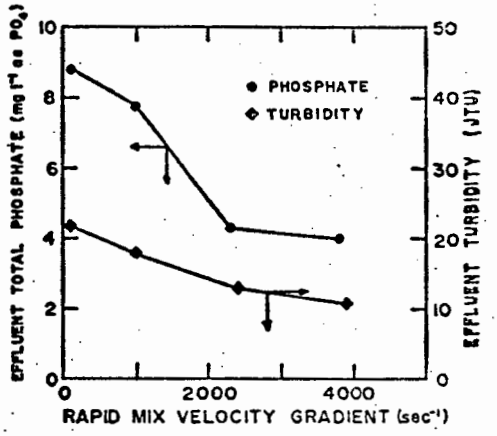

Figure 2.9. Effect of mixing intensity on the quality of lime-treated primary effluent (After MENNELL *et al*, 1974)

The second method investigated was the use of a "split feed". This term refers to the addition of the entire lime slurry feed stream to a portion only of the influent streams (the "split"), which is followed by the blending of the split stream lime mixture with the remainder of the waste stream during rapid mixing. Their rationale for this scheme was :

(1) a greater chemical driving force for lime dissolution due to the higher lime slurry concentration, and

(2) longer lime dissolution time in the "split" mixing chamber.

Their results indicated that a split stream fully saturated with lime, i.e. 12,5 percent of total flow in their particular study, produced optimal ortho-phosphate and turbidity removals.
A further implied conclusion was that optimum split feed can produce better total system performance than direct slurry feed under equivalent mixing conditions. Although the authors clearly indicated the benefits of "split feed", they did not indicate what additional capital and running costs would be and whether these would off-set the benefits of increased phosphate and turbidity removal.

Merrill (1974) reported on both batch and continuous lime precipitation of raw sewage in the system described above. The study was aimed at establishing the reaction time required for achieving essentially stabilized concentrations of PO_{4_T}, Ca_T, CO_{3_T} and Mg_T in lime-treated raw sewage. Sludge was not recirculated in this system, probably because phase separation was achieved by flotation. Typical batch test results are illustrated in Figure 2.10. Merrill concluded that batch calcium phosphate precipitation was rapid and essentially complete within 1½ minutes. Fluctuations in Ca_T and CO_{3_T} occurred within a narrow range (about 30 mg ℓ^{-1} as $CaCO_3$) upto approximately 24 minutes. Magnesium concentrations appeared to be stabilized within 4-10 minutes.

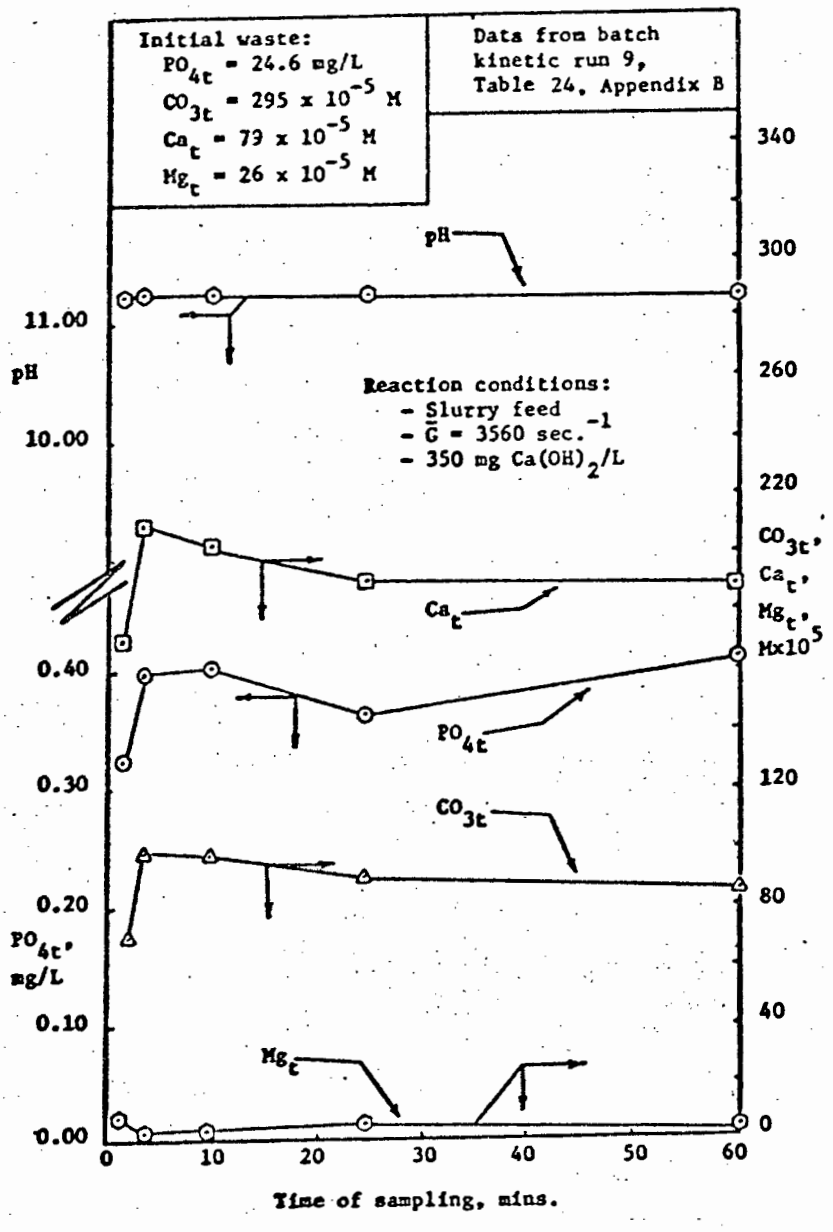

Figure 2.10. Batch lime - raw sewage precipitation (After MERRILL, 1974)

Merrill pointed out that the reaction times required for the lime precipitation reactions in batch reactors are not necessarily valid for continuously stirred tank reactor (CSTR) systems, normally used in practice. He referred to Levenspiel (1972) who has demonstrated from kinetic theory that a 1:1 correspondence between the time required to achieve a given conversion in batch systems and the nominal liquid detention time to attain the same conversion in CSTR systems, does not usually exist. Merrill used the data obtained from his pilot plant experiments (as described above) to establish CSTR residence time(s) required for achieving essentially stabilized PO_{4_T}, Ca_T, CO_{3_T} and Mg_T concentrations. Typical results are illustrated in Figure 2.11. Merrill concluded that essentially complete reactions, "an equilibrium type state", may be attained in a CSTR within 10 minutes for most systems and 30 minutes for all systems (without sludge recirculation or addition).

The use of four reaction chambers and a total residence time of 30 minutes is possibly excessive for full-scale application. Further investigations for reducing the number of reaction chambers and the reaction time appear to be necessary. The pilot plant method of Merrill is not well suited for studying the effects of precipitation reaction time behaviour. A systematic study using one (or more) reaction vessels with a range of residence times appears to offer a better opportunity for arriving at optimum CSTR residence times for lime induced reactions. Increasing the concentration of sludge in the reaction vessel by recirculation should significantly reduce the reaction time required for attaining essentially stabilized effluents. Recycling of sludge is not so advantageous in flotation processes (as the air requirements increase with the sludge concentration), but should be applicable to reaction systems preceeding sedimentation processes.

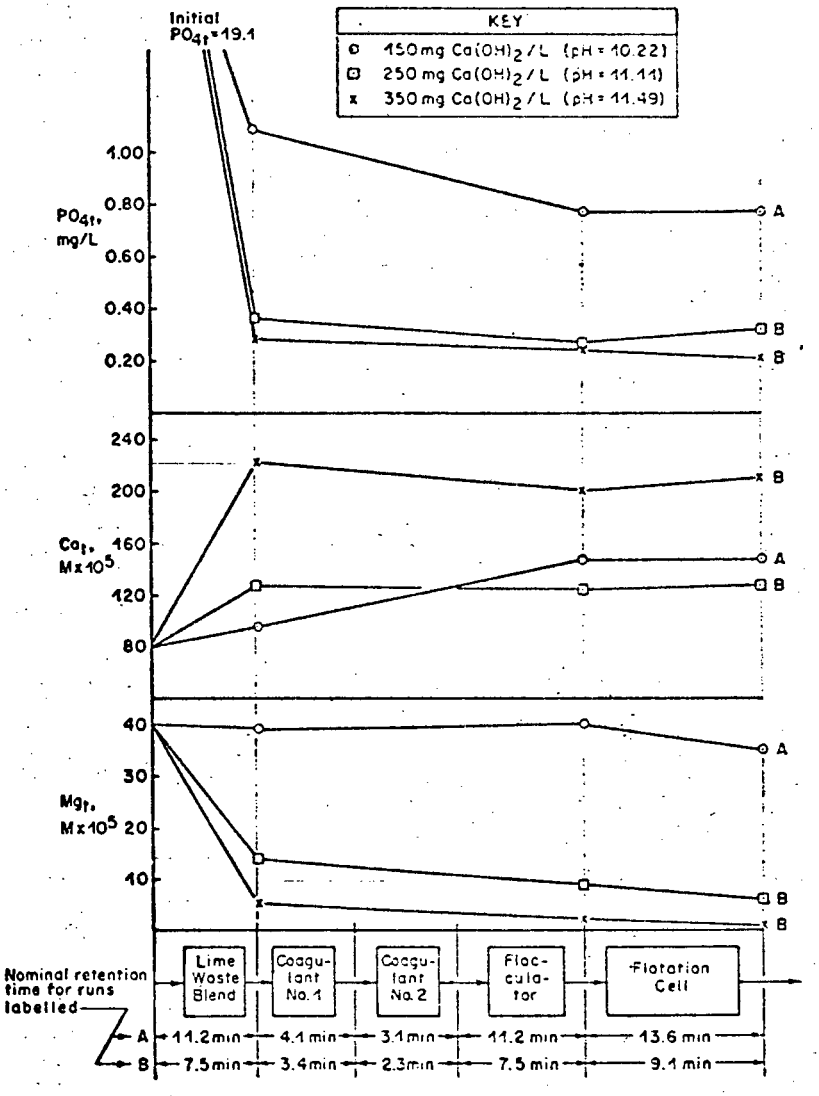

Figure 2.11. Continuous lime - raw sewage precipitation (After MERRILL and JORDEN, 1975)

In conclusion, the findings reported by Mennell, Merrill and Jorden (1974a, b; 1975) stressed the importance of optimized rapid mixing, out-lined the benefits of "split-feed" lime treatment and proposed $\bar{G}.t$ values required for the flocculation of lime-treated primary effluents. Their work indicates the need for further investigations of the time behaviour (kinetics) of lime-effluent reactions.

Jenkins and Lee (1976) investigated lime precipitation of raw municipal waste water by jar tests and on a pilot plant. Jar tests were conducted to establish the effect of the lime slurry concentration (2 to 100 g ℓ^{-1}) on raw waste water treatment at any specific lime dosage. Typical results are shown in Figure 2.12. It is clear from this figure that the lime slurry concentration dramatically affects the residual turbidity of the lime-treated raw wastewater. The authors concluded that high concentration lime slurries require longer times to dissolve in waste water than do lower concentration lime slurries.

To test this hypothesis a batch study was made of lime dissolution in various synthetic solutions and raw waste water. The following first order rate equation was fitted to the experimental data,

$$\frac{d[OH^-]/[OH^-]_\infty)}{dt} = k.\frac{[OH^-]}{[OH^-]_\infty} \quad \ldots\ (2.55)$$

The integrated form of this rate equation is,

$$\log\ (1 - [OH^-]/[OH^-]_\infty) = k.t \quad \ldots\ (2.56)$$

where $[OH^-]$ = the hydroxide ion concentration at time t

$[OH^-]_\infty$ = the equilibrium hydroxide concentration ($t \to \infty$)

Experimental results are illustrated in Figure 2.13.

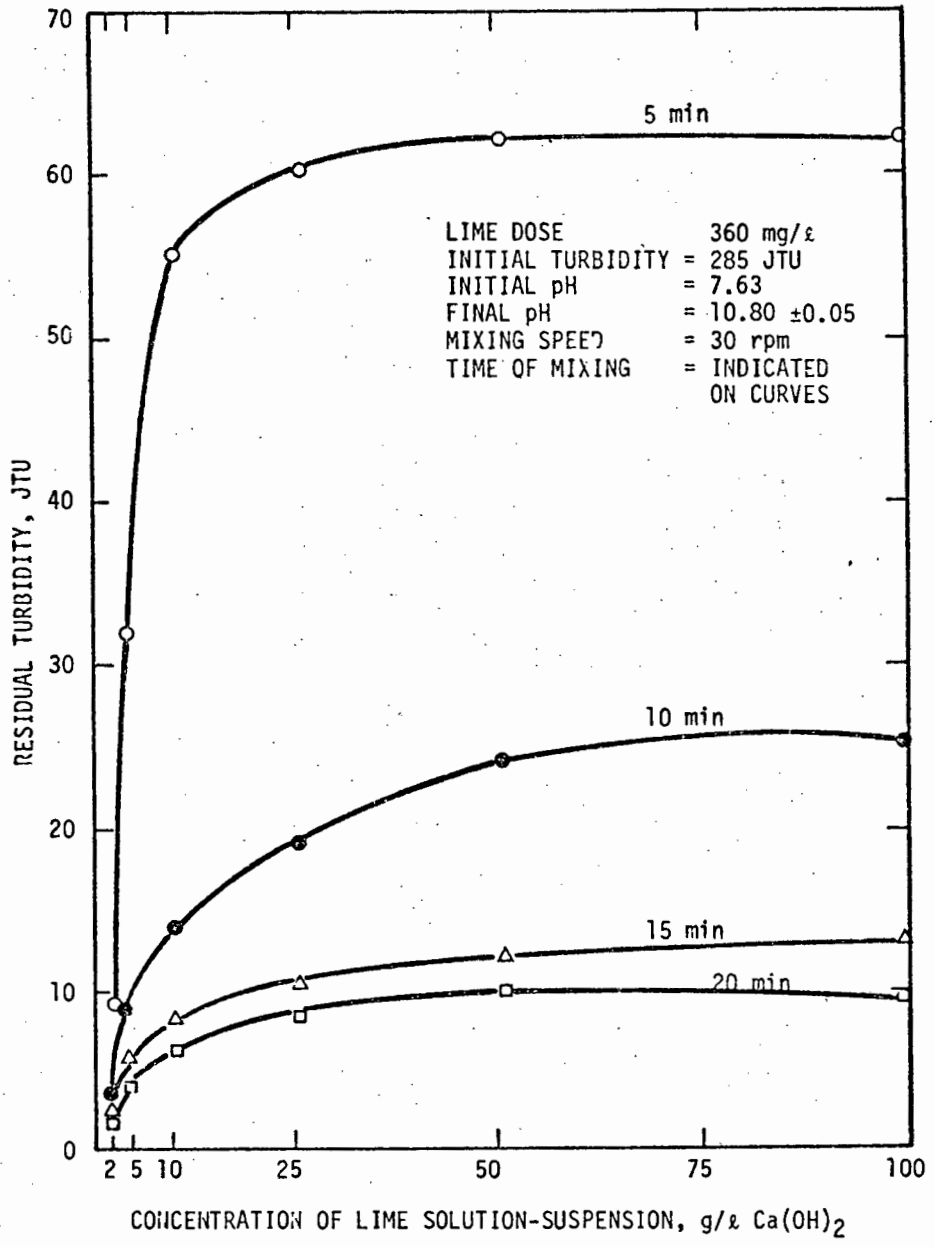

Figure 2.12. Effect of the concentration of lime solution-suspensions on the clarification of raw sewage in jar tests (After JENKINS and LEE, 1976)

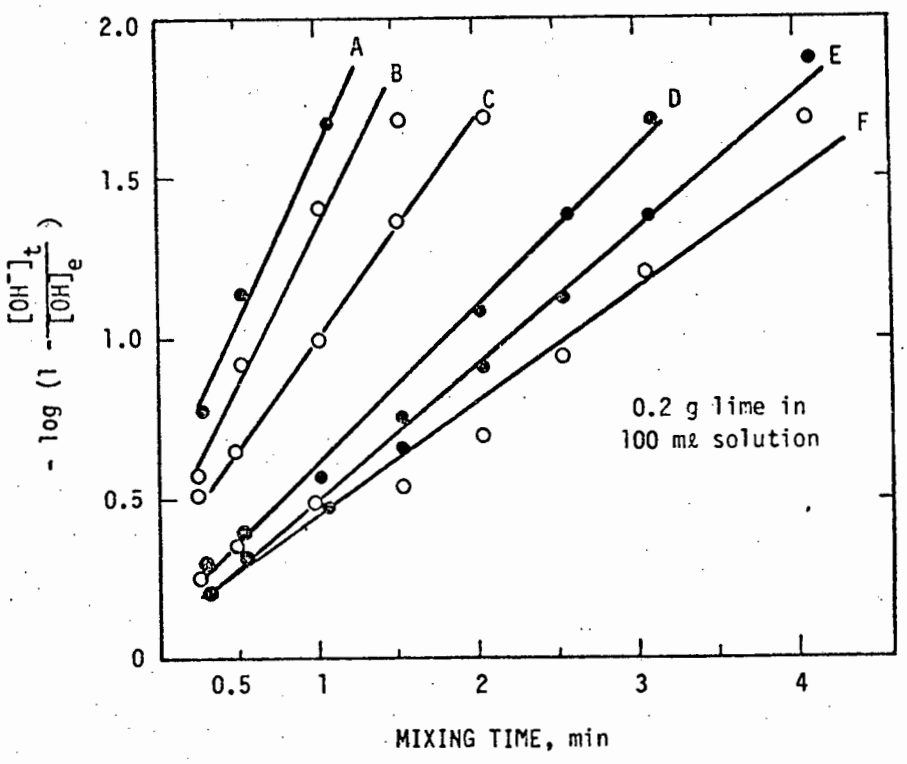

Figure 2.13. Lime dissolution rate in : A, lime-treated sewage (pH 11,1); B, distilled water; C, $MgCl_2$ solution (2 meq ℓ^{-1}); D, filtered raw sewage; E, raw sewage (alkalinity = 4.4 meq ℓ^{-1}, Mg= 2 meq ℓ^{-1}); F, Na_2CO_3 solution (5 meq ℓ^{-1}) (After JENKINS and LEE, 1976)

The integrated rate Equation, Eq. (2.56), reasonably fits the experimental data and may thus be considered an acceptable model for lime dissolution. The authors concluded that lime dissolution is severely retarded in raw waste water and Na_2CO_3 solutions (5 meq ℓ^{-1}), and slightly retarded in $MgCl_2$ solutions (2 meq ℓ^{-1}). They suggested that the dissolution rate is controlled by alkalinity which forms insoluble substances at the surface of the lime particles.

Jenkins and Lee (1976) also conducted pilot scale tests to assess the value of their batch-scale test results. They made a week-long comparative study of direct lime addition (50 g ℓ^{-1} as $Ca(OH)_2$) and lime addition to recycled clarifier effluent constituting 13,3 percent of the total flow, on a pilot plant treating waste water at 0,34 $m^3 h^{-1}$. Typical plant performance results are given in Figure 2.14, illustrating the superior performance of the second mode of operation. The improvements are attributed to better lime dissolution in this mode of operation. The authors indicated cost savings of 1,49 US \$ $M\ell^{-1}$ for a 379 $M\ell\ d^{-1}$ plant.

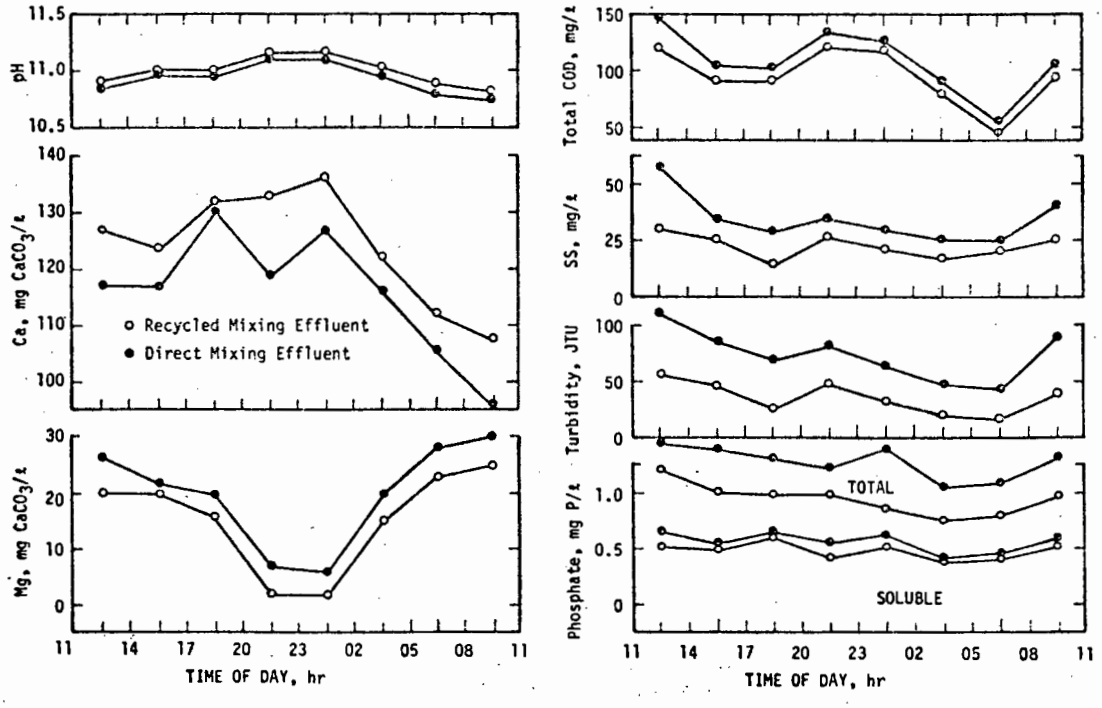

Figure 2.14. Comparative performance of direct lime addition with addition to recycled clarifier effluent (After JENKINS and LEE, 1976)

Jenkins and Lee (1976) further developed the work reported by Merrill *et al* (1974) on split lime treatment by performing more detailed studies. Jenkins and Lee confirmed the speculation by Merrill *et al* that the reason for improved turbidity and phosphate removals, using split treatment as against direct treatment, is a result of improved lime dissolution in the split stream. This was verified by studying the kinetics of lime dissolution. Lime dissolution was shown to be relatively slow and apparently inhibited by precipitation of $CaCO_3$ at the dissolving lime particle-water interface. Since dissolved lime is the reactive species which results in phosphate precipitation and turbidity removal, the slow dissolution of lime was indicated as the controlling reaction.

The rate equation for lime dissolution, Eq.(2.55), proposed by Jenkins and Lee is a simple model which has a number of drawbacks which are apparent when studying Figure 2.13. The experimental data does not strictly plot out in straight lines, nor do the fitted straight lines pass through the origin as required by Eq. (2.56). One of the reasons for the inadequacy of this model is that Equation (2.56) lacks a surface area term. Surface area in a dissolution experiment changes from a finite area to zero area when all the lime dissolves. The stage in the dissolution process just before complete dissolution, i.e. where the changes in surface area will be significant, is of greatest interest for the lime treatment process since complete dissolution is required in this process. Modelling this stage presents a formidable problem. The authors reported lime dissolution studies for 2000 mg $Ca(OH)_2$ ℓ^{-1}. However, from a practical point of view, it will be of interest to study lime dissolution kinetics for lime concentrations conventionally used in wastewater treatment, i.e. 200-600 mg $Ca(OH)_2$ ℓ^{-1}. Jenkins and Lee did not consider the effect of mixing (turbulence) on the lime dissolution reaction. If the dissolution reaction is diffusion controlled, the mixing intensity will play a major role in the dissolution kinetics.

Table 2.4

Better known large-scale plants employing lime treatment

SITE	EFFLUENT BEING TREATED	FLOW ($m^3 d^{-1}$)	REFERENCE
Contra Costa Central Sanitary District	Raw Sewage	9323	Parker (1972)
Dan Region	Secondary Effluent	43000	Idelovitch *et al* (1976)
Orange County District	Secondary Effluent	56800	Argo and Montes (1975)
Pretoria	Secondary Effluent	4550	Van Vuuren and Henzen (1972)
South Tahoe	Secondary Effluent	28425	Culp and Culp (1971)
Windhoek	Maturation Pond Effluent	4500	S A Water Bulletin (1976)

5.3 Lime-Treated Waste Water - Large-Scale Plants

In recent years the lime treatment process is more frequently being used to upgrade sewage effluents, specifically in water reclamation plants. Table 2.4 lists a number of the better known large-scale plants where lime treatment is being used.

All the large-scale plant experiments reported in this thesis were conducted on the Stander Water Reclamation Plant at Pretoria, South Africa. This plant was commissioned towards the end of 1970. The design of the plant was based on extensive laboratory-and pilot-scale studies by the National Institute for Water Research (Council for Scientific and Industrial Research, Pretoria, South Africa) and full-scale reclamation

studies at Windhoek (South West Africa).

Van Vuuren, Stander, Henzen, Meiring and Van Blerk (1967) reported some of these pilot plant (4,1 $M^3 h^{-1}$) results obtained by a system of combined lime softening and dispersed air flotation. A flocculation-flotation process was chosen for its low residence time of 20 minutes, compared with a retention time of 3 to 4 hours in a conventional sedimentation process. The authors attributed the success of this process to the entrainment of air and finely dispersed $CaCO_3$ by the magnesium hydroxide floc which formed as a result of pH elevation by lime addition to the effluent. The optimum pH values for flocculation of primary and secondary humus tank effluent were reported as 11,4 and 11,2, respectively. The authors stressed that flash mixing of lime and effluent was essential for the effective use of the lime. Unfortunately no design details were specified in their paper.

Van Vuuren and Henzen (1972) reported on the commissioning and first year's operation of the Stander Plant. The flotation unit, the design of which was based on the pilot plant work mentioned above, gave disappointing results. There were two reasons for poor flotation on the large-scale plant,

(1) The commissioning of the full-scale plant coincided with the introduction of soft detergents. As a consequence the detergent concentration in the effluent decreased to a marked degree and this reduced the air-particle adhesion properties.

(2) Dispersed air flotation worked well on the pilot plant but appeared ineffectual on the large scale plant. At that time the advantages of dissolved air flotation had not yet been recognized.

The authors mentioned that the removal of supersaturated calcium carbonate conditions was a factor of major importance in order to safeguard against excessive scaling in the ammonia stripping tower. This paper gives a useful review of the Stander Plant's commissioning and subsequent operation. However, since the main emphasis is on process selection and the cost of advanced waste water treatment, it did not deal in depth with aspects related to $CaCO_3$ and $Mg(OH)_2$ precipitation.

Wiechers (1973) reviewed the problems associated with $CaCO_3$ and $Mg(OH)_2$ precipitation in the Stander Water Reclamation Plant. Several areas of major concern were identified,

(1) There existed a lack of knowledge regarding the conditions necessary for optimal $CaCO_3$ and $Mg(OH)_2$ precipitation.

(2) Reigning operational conditions resulted in an unstable clarifier effluent which gave rise to scale formation in pumps, piping and in the process units following the high lime process, i.e. equalization pond and ammonia stripping tower.

The review indicated that although the process configurations showed great potential, this could not be fully realized until the fundamental and practical aspects relating to the problem of $CaCO_3$ and $Mg(OH)_2$ precipitation were resolved.

Many studies of full-scale lime treatment have been reported in the literature. Unfortunately here also very little data is available on $CaCO_3$ and $Mg(OH)_2$ precipitation. Most of the studies reported on full-scale plants deal mainly with aspects related to organic matter and phosphate removal and clarification. However, useful results relating to the lime treatment process as an integral part of a reclamation process at South Tahoe have been published in

book form (Culp and Culp, 1971). This book has been updated several times in the form of seminar notes which deal with the latest world-wide technological developments in this field. The information thus collected has been incorporated into a set of design guidelines (Culp, Wesner, Culp and Benjes, 1975). Guidelines specifically related to lime treatment and hence $CaCO_3$ and $Mg(OH)_2$ precipitation are,

(1) "Adequate rapid mixing of this coagulant (lime) and the waste water must be provided. High turbulence areas such as Parshall flumes in existing plants may be suitable. New plants should include specifically designed rapid mix basins. Scum and foam control should be provided".

(2) "Provisions should be made to add polymer at the point of coagulant addition and at several points downstream of coagulant addition."

(3) "Transport time from the rapid mix basin to the flocculation basin should be minimized (less than one minute)".

(4) "Mechanical air flocculation must be provided. Hydraulic flocculation devices are not desirable due to localized areas of high energy concentration and lack of flexibility. Typical with the large coagulant dosages needed for phosphorus removal, flocculation times of 5 minutes are adequate. However, flocculation time should be evaluated for each specific wastewater in laboratory or pilot tests. Flocculation times observed as adequate in jar tests should be multiplied by a scale up factor of 2 for full-scale design."

(5) A design parameter, the temporal mean velocity gradiant, G, was specified for flocculation units, i.e.

$$G = (P/uV)^{\frac{1}{2}} \quad \ldots\ldots \quad (2.57)$$

where P = power input (ft-lb/sec)
u = absolute viscosity of water (lb-sec/ft^2)
V = volume of basin (ft^3)

Another parameter which has been used in flocculation basin design is G.t, where t is the detention time in the flocculation basin. Values of G for wastewater treatment have varied between 10 and 200 ft/sec/ft, with G.t ranging between 10^4 to 10^5.

(6) "The flocculation basin should have inlet ports that create a headloss at least 10 times greater than the transport headloss to provide good flow distribution to the flocculation basin."

(7) "The flocculation basin should have a means for positive scum removal."

(8) "The flow from the flocculation basin must not be subjected to excessive turbulence which would disrupt the floc."

(9) "Provisions should be made for returning solids from the primary clarifier to the flocculator."

(10) "Primary clarifier overflow rates should be the same as for conventional basins. When using lime, higher rates may be possible but these should be demonstrated in pilot studies before being used in design. Overflow rates should not exceed 1000 gpd/sq.ft on a daily average basis or more than 1400 gpd/sq.ft at peak hourly flow. Calculations of overflow rates must include external recycle flows to the chemical clarifier."

Some of these design guidelines are rather non specific and require further quantitative statements if they are to be used as sound guidelines for design. Specific points in question are :

(1) The authors do not specify what is meant by "adequate" rapid mixing. Here it may be useful to apply the criterion suggested by Merrill (1974), i.e. $\bar{G} = 600\ sec^{-1}$. The objective of rapid mixing in lime treatment is not only to mix the lime adequately with the effluent, but to dissolve the lime completely and ensure that the precipitation reactions go to completion. If this is not the case, precipitation will take place in the flocculation unit and clarifier, possibly resulting in a turbid unstable effluent.

(2) Adequate guidelines for flocculation basin design are given, indicating that for optimal design purposes a pilot plant study of lime treatment for a specific effluent is essential.

(3) The importance of sludge recirculation is stressed. However, no guidelines are given for the optimum sludge concentration or sludge age. The effect of sludge reciruclation on flocculation is not discussed.

(4) Basic guidelines for the clarification stage were specified. However, no indication was given as to the preferred clarifier design, i.e. conventional sedimentation tanks, solid contact clarifiers or sludge blanket clarifiers.

Some of the design features of the full-scale plant (28,4 Mℓ d^{-1}) at South Tahoe have been described by Culp and Culp (1971). The rapid mix basin for mixing lime with secondary effluent provides about one minute of mixing at design flow. A vertical shaft mixer is used. (Figure 2.15). They reported that lime deposits build up on the metal mixer paddles, which required frequent cleaning to avoid shaft vibration. The authors specified the following design guidelines for rapid mixing,

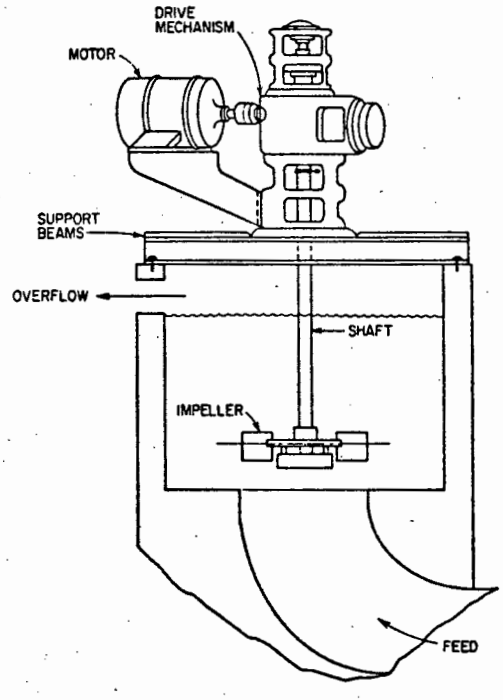

Figure 2.15. Mechanical rapid-mixing device (After CULP and CULP, 1971)

(1) The rapid mixing basin should be equiped with a high speed mixing device capable of creating velocity gradients of 300 fps/ft or more.

(2) The rapid mixing basins should have a detention time of 15-60 seconds.

(3) Power requirements to satisfy (1) and (2) would require 0,25 to 1,0 hp/MGD.

At South Tahoe the rapid mix basins are followed by flocculation basins with five minutes detention time.

Argo and Montes (1975) have described the lime treatment process at the full-scale water reclamation plant (56,8 Mℓ d^{-1}) in Orange County, USA. An isometric sketch of the lime treatment unit is reproduced in Figure 2.16. Design details are as follows :

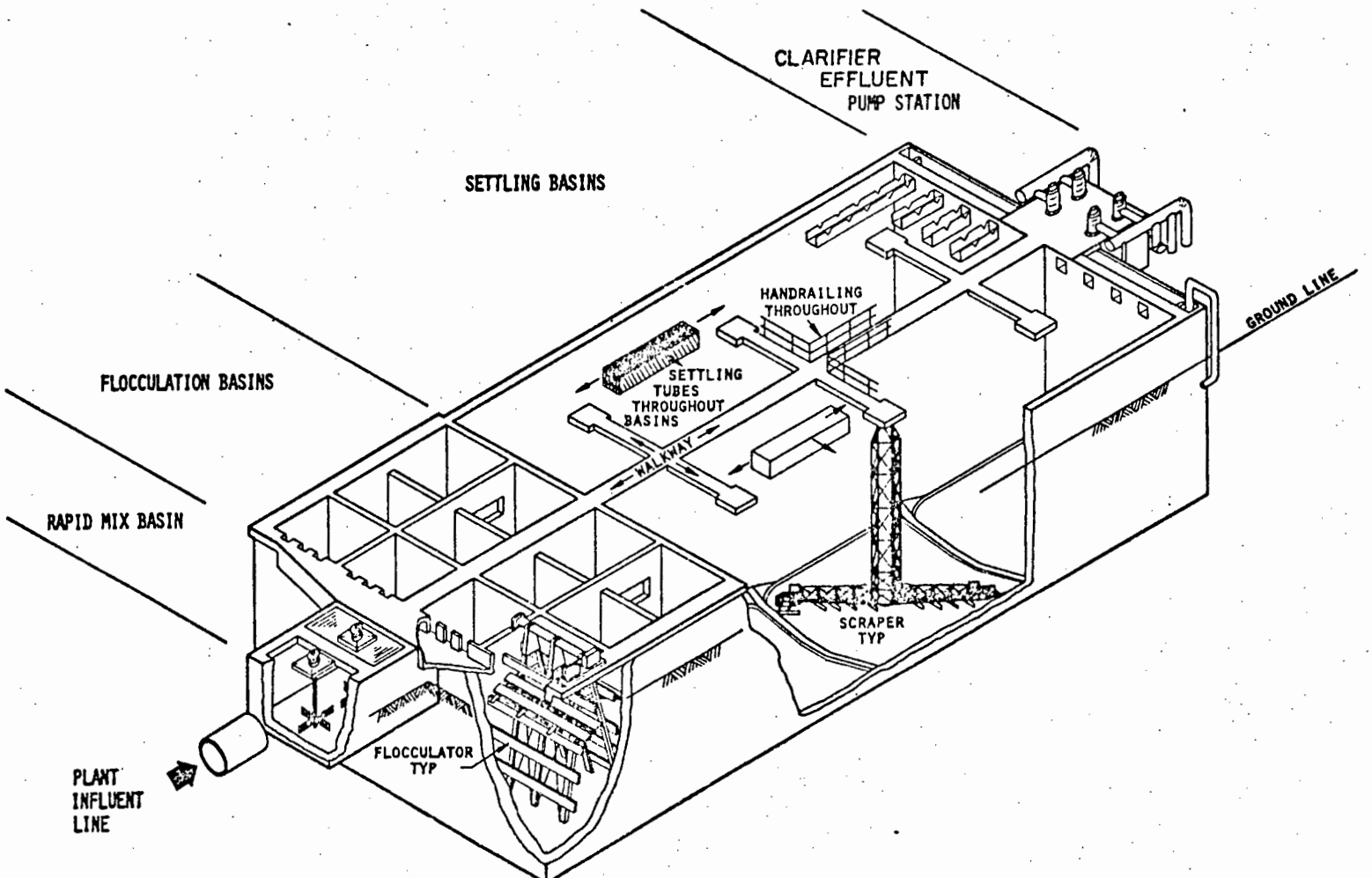

Figure 2.16. Orange County (USA) secondary effluent lime treatment plant (After ARGO and MONTES, 1975)

(1) Rapid mixing

Number of basins : 2 in series
Mechanical mixer in each basin
Dimensions : 12x12x12 ft^3
Detention time : 2,4 minutes at 15 mgd
Chemical addition : First basin - lime, alum, recycled lime sludge
Second basin - polymer

(2) Flocculation :

Number of basins : 2, three compartments each
Detention time : 10 min/compartment (30 min. total) at 15 mgd
Chemical addition : Polymer, 1st and 3rd compartments
Dimensions : 48x41x11 ft^3
Flocculator mechanism : oscillating type

(3) Settling Basins :

Number of basins : 2 rectangular
Dimensions : 120x40x11 ft^3
Surface overflow rate : 1563 gpd/sqft at 15 mgd
Each basin was equipped with settling tubes

Results reported for this system dealt mainly with turbidity, COD and phosphate removal, all of which were excellent. However, no mention was made of $CaCO_3$ and $Mg(OH)_2$ precipitation, or if the water was stable after clarification. In addition, no reasons were mentioned for the choice of the above design parameters. However, it is interesting to note that the design is conservative compared to the South Tahoe design, i.e. rapid mixing detention time of 2 minutes as against 1 minute, and flocculation time of 30 minutes as against 5 minutes.

Design details for the lime treatment process of the Stander Reclamation plant will be dealt with in Chapter 5.

It is clear from the above that there already exists a large body of knowledge regarding the lime treatment process as applied to waste waters. However, there is a lack of knowledge relating to the aspects of $CaCO_3$ and $Mg(OH)_2$ precipitation. Design guidelines regarding these aspects of the process seem to be most urgently required, since the production of an unstable and turbid water may cause serious problems downstream of the lime treatment process.

6. CONCLUSIONS

The review dealt with the pertinent literature which exists on calcium carbonate and magnesium hydroxide precipitation. It also delineated the aspects which require further investigation. The major conclusions may be summarized as follows :

(1) The equilibrium (or apparent equilibrium) behaviour of calcium carbonate and magnesium hydroxide precipitates in lime-treated effluent is not clearly understood.

(2) Predictive models such as the Modified Caldwell-Lawrence Diagram have limited application to lime-treated effluents. Development of "apparent equilibrium constants" for $CaCO_3$ and $Mg(OH)_2$ to replace the thermodynamic equilibrium constants of calcite and brucite used in the Diagram, may overcome this problem. If such an extention of the model is possible it will greatly extend the practical value of the Diagram.

(3) Although a number of studies have been reported in the literature on calcium carbonate precipitation kinetics in pure systems, none of these studies dealt with conditions representative of "real life" lime treatment and recarbonation processes.

(4) Most of the studies on the lime treatment of waste water deal with the aspects of phosphate and organic matter removal and coagulation. Little or no attention is given to the calcium, magnesium and carbonate systems. A need for characterizing lime-treated effluents in terms of the relationships between pH and lime dosage, residual dissolved calcium and magnesium, alkalinity and sludge generation is indicated.

(5) Existing guidelines for the design of lime treatment processes indicate a need for more specific information on design aspects relating to $CaCO_3$ and $Mg(OH)_2$ precipitation.

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CHAPTER 3

PURE SYSTEM $CaCO_3$ PRECIPITATION

1. INTRODUCTION

Calcium carbonate precipitation kinetics for the lime-waste water system have not been studied in any depth, as indicated in the literature review in Chapter 2. Synthetic system $CaCO_3$ precipitation kinetics have been reported in the literature, the most extensive work being that of Reddy and Nancollas (1971). As outlined in the literature survey, the rate equation they propose (Eq. 2.30) forms a useful starting point for any further work on $CaCO_3$ precipitation kinetics. To be of value in this specific study, the validity of Eq. (2.30) has to be established for synthetic solutions with pH values, alkalinity and calcium concentrations which are commonly encountered in lime treatment and softening. In practice these processes are usually operated with high rates of precipitation, whereas Eq. (2.30) was developed for slow rates. Referring to the criticisms levelled at the Reddy and Nancollas equation (see Chapter 2, Section 3.4), it would be injudicious to accept their formulation at these higher rates and concentrations without verifying the applicability of their equation. A further constraint in applying the rate Equation (2.30) is that it was developed to describe batch precipitation of $CaCO_3$, whereas in practice water treatment processes are usually continuous. Synthetic system studies are therefore necessary to establish the validity of Eq. (2.30) for continuous $CaCO_3$ precipitation.

It is realized that synthetic system studies may not be directly applicable to real life systems. However, such studies may form a useful basis for qualitative predictions of the effects of parameters such as the degree of supersaturation, sludge concentration, reactor residence time, temperature and mixing intensity. The form of the rate equation developed for these synthetic systems could also be used as the empirical form for modelling real life systems.

2. CALCIUM CARBONATE PRECIPITATION THEORY

When attempting to study the precipitation kinetics of $CaCO_3$, a major problem is to determine the quantity of $CaCO_3$ that has precipitated up to a particular time. The reaction rates can be so rapid that it is difficult to identify the particular time corresponding to a particular measurement. Also, if large seed masses are employed, the mass growth is small with respect to the mass already present and it will be difficult to obtain accurate results from mass differences. Furthermore, to measure mass requires precipitate separation from the liquid phase by say filtration or centrifugation, which introduces an indeterminant time element and may change the condition(s) of precipitation during the separation operation, e.g. the CO_2 partial pressure may change which may either speed-up or reduce the rate of precipitation.

A solution to this problem is to utilize the equilibrium theory for the carbonic-calcium system. Employing this approach it can be shown (see below) that during the course of a precipitation experiment only two measurements need to be made in order to define completely the state of the reaction. Reddy and Nancollas (1971) measured the pH and residual total dissolved calcium, Ca_T^{2+}, in the solution. Whereas pH measurement can be readily made, the problem of Ca_T^{2+} measurement in a rapidly precipitating system still remains. Reddy and Nancollas (1971) used this method effectively, as they worked with low supersaturation states where precipitation was not rapid and fairly accurate Ca_T^{2+} measurements with time could be made.

After a thorough study of the carbonic-calcium system it was concluded that provided the pH in an experiment does not exceed approximately 10, the concentration of the $CaOH^+$ ion pair is very small compared to those of the other ions in solution. Neglecting the $CaOH^+$ ion pair reduces the number of variables by one and allows determination of all the variables of the system by monitoring only the pH. By this means it is possible to record the pH-time curve in any precipitation experiment and calculate the time relationships for any parameter of the system. Once

these relationships are available it is possible to test any proposed kinetic theory for the rate of $CaCO_3$ precipitation against the experimental values and thereby test the applicability of the proposed kinetic theory.

2.1 Equilibrium Equations

The following three sets of equilibrium relationships must be taken into account in solutions from which calcium carbonate precipitates (Reddy and Nancollas, 1971) :

Carbonic Species and Water Equilibria,

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad .... \quad (3.1)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad .... K_1 .... \quad .... \quad (3.2)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad .... K_2 .... \quad .... \quad (3.3)$$

$$H^+ + OH^- \rightleftharpoons H_2O \quad .... K_w .... \quad .... \quad (3.4)$$

Ion Pair Equilibria (Only the ion pairs considered to have significant effects in this process are considered),

$$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+ \quad .... K_{CaHCO_3^+} ... \quad .... \quad (3.5)$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^o \quad .... K_{CaCO_3^o} ... \quad .... \quad (3.6)$$

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \quad .... K_{CaOH^+} ... \quad .... \quad (3.7)$$

Solubility Product,

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(S) \quad \cdots K_{sp} \cdots \quad \ldots\ldots (3.8)$$

The K values given above are the thermodynamic equilibrium constants for the carbonic and calcium systems in pure water. Using mass action concepts the relationships between the K values and the species concentrations are as follows :

$$\frac{[H^+][HCO_3^-].f_M^2}{[H_2CO_3^-]} = K_1 \quad \ldots\ldots (3.9)$$

$$\frac{[H^+][CO_3^{2-}].f_D}{[HCO_3^-]} = K_2 \quad \ldots\ldots (3.10)$$

$$[H^+][OH^-].f_M^2 = K_w \quad \ldots\ldots (3.11)$$

$$\frac{[Ca^{2+}][HCO_3^-].f_D}{[CaHCO_3^+]} = K_{CaHCO_3^+} \quad \ldots\ldots (3.12)$$

$$\frac{[Ca^{2+}][CO_3^{2-}].f_D^2}{[CaCO_3^o]} = K_{CaCO_3^o} \quad \ldots\ldots (3.13)$$

$$\frac{[Ca^{2+}][OH^-].f_D}{[CaOH^+]} = K_{CaOH^+} \quad \ldots\ldots (3.14)$$

$$[Ca^{2+}][CO_3^{2-}].f_D^2 = K_{sp} \quad .... \quad (3.15)$$

and

$$pH = \log ([H^+].f_M) \quad .... \quad (3.16)$$

where [ ] = designates concentration (mol ℓ^{-1})
f_M = activity factor for monovalent ions
f_D = activity factor for divalent ions

The activity factors are calculated from the Davies equation (Davies, 1967),

$$-\log f_M = 0,51.1.1 \left\{\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0,30.I\right\}$$
$$= 0,51.F(I) \quad .... \quad (3.17)$$

and

$$-\log f_D = 2,04.F(I) \quad .... \quad (3.18)$$

where

$$F(I) = \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0,30.I \quad .... \quad (3.19a)$$

and

$$I = 0,5\Sigma Z_i^2 C_i \quad .... \quad (3.19b)$$

where I = Ionic strength of solution (mol ℓ^{-1})
Z_i = Ionic charge of the ith ion in solution
C_i = concentration of the ith ion in solution (mol ℓ^{-1})

2.2 Assumptions

In the development of the kinetic relationships the following assumptions are made :

(1) The ionic equilibria described by Eqs. (3.2), (3.3) (3.4) (3,5) (3.6) and (3.7) are attained very rapidly on mixing solutions containing carbonic and calcium species and the reactions can be taken as complete within milliseconds. For calculational purposes the attainment of these equilibria is assumed to be instantaneous.

(2) The equilibrium described by Eq. (3.8) is attained slowly, i.e. the rate of calcium carbonate precipitation is relatively slow as compared to the rate of ionic reactions in solution.

(3) In the pH range 8 to 10, which is the range studied in this section, and at relatively low calcium and carbonic species concentrations (10^{-2} mol ℓ^{-1}), the concentration of the ion pair $CaOH^+$ is small compared to the concentrations of Ca^{2+}, $CaCO_3^o$ and $CaHCO_3^+$ and can be neglected.

The following example illustrates the significance of the $CaOH^+$ ion pair. Consider a solution with the following species concentrations,

Total Calcium = $1{,}223 \times 10^{-3}$ mol ℓ^{-1}
Total carbonic species = $1{,}540 \times 10^{-3}$ mol ℓ^{-1}
Solution pH = 9,87

Using the thermodynamic dissociation constants $K_{CaCO_3^o}$, $K_{CaHCO_3^+}$ and K_{CaOH^+}, the concentrations of the various calcium species can be calculated, i.e.

$[Ca^{2+}] = 9{,}43 \times 10^{-4}$ mol ℓ^{-1}
$[CaCO_3^o] = 2{,}84 \times 10^{-4}$ mol ℓ^{-1}
$[CaHCO_3^+] = 0{,}114 \times 10^{-4}$ mol ℓ^{-1}
$[CaOH^+] = 0{,}015 \times 10^{-4}$ mol ℓ^{-1}

From the above results the concentration of $CaOH^+$ is negligible compared to the concentrations of Ca^{2+}, $CaCO_3^o$ and $CaHCO_3^+$. Hence, at pH values lower than 10 neglecting the ion pair $CaOH^+$ may bring about errors in the order of 0,1 to 0,2 percent which is well within the experimental accuracy (5 to 10 percent).

2.3 Establishment of the Initial or Supersaturated State

The initial state is defined as the state of the solution immediately after the stock solutions have been mixed, but precipitation has not yet commenced. This is an ionic state, and is described by Eqs. (3.9), (3.10), (3.11), (3.12), (3.13), (3.17), (3.18), (3.19) and the following equations :

Equation for electro-neutrality,

$$[CaHCO_3^+] + [Na^+] + [H^+] + 2[Ca^{2+}] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-] \quad \ldots\ (3.20)$$

Equation for total carbonic species,

$$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [CaCO_3^o] + [CaHCO_3^+] \quad \ldots\ (3.21)$$

Equation for ionic strength,

$$I = 0{,}5.\{[H^+] + [Na^+] + 4[Ca^{2+}] + [OH^-] + 4[CO_3^{2-}] + [HCO_3^-] + [Cl^-] + [CaHCO_3^+]\} \quad \ldots\ldots \quad (3.22)$$

Equation for total calcium species in solution,

$$[Ca_T^{2+}] = [Ca^{2+}] + [CaCO_3^o] + [CaHCO_3^+] \quad \ldots\ldots \quad (3.23)$$

The above twelve equations contain twentyone variables,

C_T; $[Na^+]$; $[Ca^{2+}]$; $[Ca_T^{2+}]$; $[Cl^-]$; $[H_2CO_3]$; $[HCO_3^-]$;
$[CO_3^{2-}]$; $[CaCO_3^o]$; $[CaHCO_3^+]$; $[H^+]$; $[OH^-]$; K_1; K_2;
K_w; $K_{CaCO_3^o}$; $K_{CaHCO_3^+}$; $F(I)$; I; f_D; f_M

There are nine known parameters and twelve independent equations which relate the twentyone variables to one another, i.e.

C_T; Na^+; Cl^-; Ca_T^{2+}; K_1; K_2; K_w; $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$
and twelve independent equations.
Hence it is theoretically possible to calculate all the unknown species concentrations for the initial state of the reaction solution ($t = 0$).

Since the ionic strength is a function of the concentrations of the ionic species and changes with crystallization, calculation by a method of successive approximations is necessary to determine both the species concentrations and the ionic strength. The computer program developed for this purpose is listed in Appendix 9.

2.4 Precipitation State

Calcium carbonate pr... lution may be represented as follows,

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \quad \ldots\ (3.24)$$

or

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^{o} \quad \ldots\ (3.25)$$

The removal of calci... on is assumed to proceed by the reaction of calcium i... ions to form the ion pair $CaCO_3^o$ and solid $CaCO_3$. H... total calcium concentration due to the precipit..., is equal to the change in total carbonic specie...

$$[Ca_T^{2+}]_i - [Ca_T^{2+}] = ([\ldots + [CaCO_3^o]_i) - ([\ldots [CaCO_3^o])$$

$$= C_{T_i}$$

$$= ([H_2\ldots [CO_3^{2-}]_i + [Ca\ldots - ([H_2CO_3] + [HC\ldots aHCO_3^+] + [CaCO_3^o]) \quad \ldots\ (3.26)$$

where $[\ ]_i$ = ...tion (mol ℓ^{-1}) at t = 0

$[\ ]$ = ...l ℓ^{-1}) at t = t

Equation (3.26) reduces to

$$[Ca^{2+}]_i - [Ca^{2+}] = ([H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{2-}]_i) - ([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]) \quad .... \quad (3.27)$$

At any time the state of the reaction solution is described by Eqs. (3.9), (3.10), (3.11), (3.12), (3.13), (3.16), (3.17), (3.18), (3.19), (3.20), (3.22), (3.23) and (3.27). These equations contain twenty-five variables,

$[H_2CO_3]_i$; $[HCO_3^-]_i$; $[CO_3^{2-}]_i$; $[Ca^{2+}]_i$; $[H_2CO_3]$; $[HCO_3^-]$; $[CO_3^{2-}]$; $[Ca^{2+}]$; $[H^+]$; $[OH^-]$; $[CaCO_3^o]$; $[CaHCO_3^+]$; $[Na^+]$; $[Cl^-]$; K_1; K_2; K_w; $K_{CaHCO_3^+}$; $K_{CaCO_3^o}$; pH; F(I); I; f_M; f_D; $[Ca^{2+}_T]$

However, there are the following known values and conditions,

(1) Initial concentrations at time zero (t = 0) are available from previous calculation,

$[H_2CO_3]_i$, $[HCO_3^-]_i$, $[CO_3^{2-}]_i$, $[Ca^{2+}]_i$, $[Na^+]$ and $[Cl^-]$

(2) Equilibrium constants,

K_1, K_2, K_w, $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$

(3) and thirteen equations of state.

Thus there are twenty-five variables with twenty-four known values or independent relationships. The twenty-fifth variable is chosen to be pH which can be measured so that the system then can be completely

solved. The reaction solution pH can be measured as the reaction proceeds. The pH must be measured with accuracy to reflect the true value, even when the reaction is fairly fast. Normally in kinetic studies the time rate at which the method of measurement (the pH) attains a steady value must be at least 10 times more rapid than the kinetic rate measured. Thus the response time of the pH probe will limit the kinetic rates that can be measured.

The unknown species concentrations are calculated from experimentally measured pH values by a method of successive approximations. The computer program, EXPDA1, used for this purpose is listed in Appendix 9.

The above theory and sequence of calculations details the procedure for determining the concentrations of all the species in solution once the pH is measured. When the species concentrations are known as functions of time, these can be used to test the particular kinetic theory favoured to explain the precipitation time behaviour.

The kinetic theory considered for batch-seeded $CaCO_3$ precipitation was that of Reddy and Nancollas (1971), (see Chapter 2, Eq. 3.30),

$$\frac{d[Ca_T^{2+}]}{dt} = k_G.S.\{[Ca^{2+}][CO_3^{2-}] - K_{sp}/f_D^2\} \quad .... \quad (3.28)$$

A plot $d[Ca_T^{2+}]/dt$ versus $S.\{[Ca^{2+}][CO_3^{2-}] - K_{sp}/f_D^2\}$ can be used to test if the model is valid, since if the data plots to a straight line through the origin, the precipitation results conform to the model given by Eq. (3.28) and the rate constant, k_G, will be given by the slope of this linear plot.

2.5 Calculation of all the Species Concentrations in Solution

If all the species concentrations in solution are to be calculated, including ion pair $CaOH^+$, it becomes necessary to measure two parameters experimentally. Reddy and Nancollas (1971) measured the total calcium concentration and pH during calcium carbonate crystallization from

supersaturated solutions.

In Eq. (3.26) the change in total calcium due to $CaCO_3$ precipitation was determined from the change in carbonic species. This allows all the species in solution to be determined, except $CaOH^+$. If $CaOH^+$ is to be determined, Eqs. (3.26 and 3.27) are no longer valid. Instead all the equations other than (3.26 and 3.27) plus an equilibrium Eq. (3.14) constitute the new system. It is now found that a number of variables cancel, but the number of parameters to be measured experimentally increases to two. The system to be solved is now

(1) Thirteen equations

(2) Eight constants,

K_1; K_2; K_w; $K_{CaCO_3^o}$; $K_{CaHCO_3^+}$; K_{CaOH^+}; Na^+; Cl^-

(3) and two measured variables, e.g. Ca_T^{2+} and pH;

3. HOMOGENEOUS $CaCO_3$ PRECIPITATION IN BATCH REACTORS

The first set of experiments conducted in this investigation were homogeneous $CaCO_3$ precipitation experiments in batch reactors. This probably is the most unlikely system to be encountered in practice. However, the experiments were intended to establish the induction periods for this process, since these could have some practical significance in processes such as the recarbonation process.

3.1 Materials and Methods

Chemical reagents

Analytical reagent grade chemicals were used throughout with MERCK brand $CaCO_3$ seed crystals for all experiments unless indicated otherwise. Carbon dioxide-free distilled water, with a conductivity less than 5 µS was used throughout. Stock solutions (0.01 M) of sodium bicarbonate, sodium hydroxide and calcium chloride were made up and standardized before each series of tests. Borax was used as a

primary standard and sulphuric acid as a secondary standard against which the sodium hydroxide and bicarbonate stock solutions were standardized, using a method of endpoint determination as set out by Loewenthal and Marais (1976). The calcium stock solutions were standardized by the EDTA method (Standard Methods, 1975).

Reactor vessel and temperature control unit

In this investigation a specially designed batch reactor was used for the study of the reaction kinetics at constant temperature ($\pm$ 0,1^{o}C) and minimal reaction solution-atmosphere contact, to minimize carbon dioxide adsorption or desorption. The reactor and other apparatus used in these experiments are shown in Figures 3.1, 3.2, 3.3, 3.4 and 3.5. A cylindrical reactor, constructed from thin perspex, was used in these experiments (see Figures 3.4 and 3.5). Its interior is sealed from the atmosphere by an O-ring sealed lid. The lid has four circular openings lined with O-rings, to allow easy air-tight insertion of the four probes, i.e. glass, calomel and conductivity electrodes and a thermometer. The lid has two additional holes, one of which allows the in-flow of reactants and a second which allows the air to escape from the reactor as the reactants displace the air. The first hole is fitted with an instrument which injects the reactants well mixed and within a period of 2 to 3 seconds (see Figures 3.1, 3.2 and 3.3).

The injector consists of two perspex cylinders (280 mℓ each), a perspex valve and a mixing chamber. After the reactants have displaced the air in the reactor (under gravity), the valve is closed to seal the system from the atmosphere. The air escape hole is fitted with a perspex stopper as soon as the reactor has been filled with reactants. The stopper has a small hole drilled through it to allow for pressure equalization in the vessel with the atmosphere, but ensures minimal solution-atmosphere contact. The reaction solution is completely insulated (electrically) from its surroundings by means of perspex and rubber O-rings to prevent stray electric currents from affecting measuring probes.

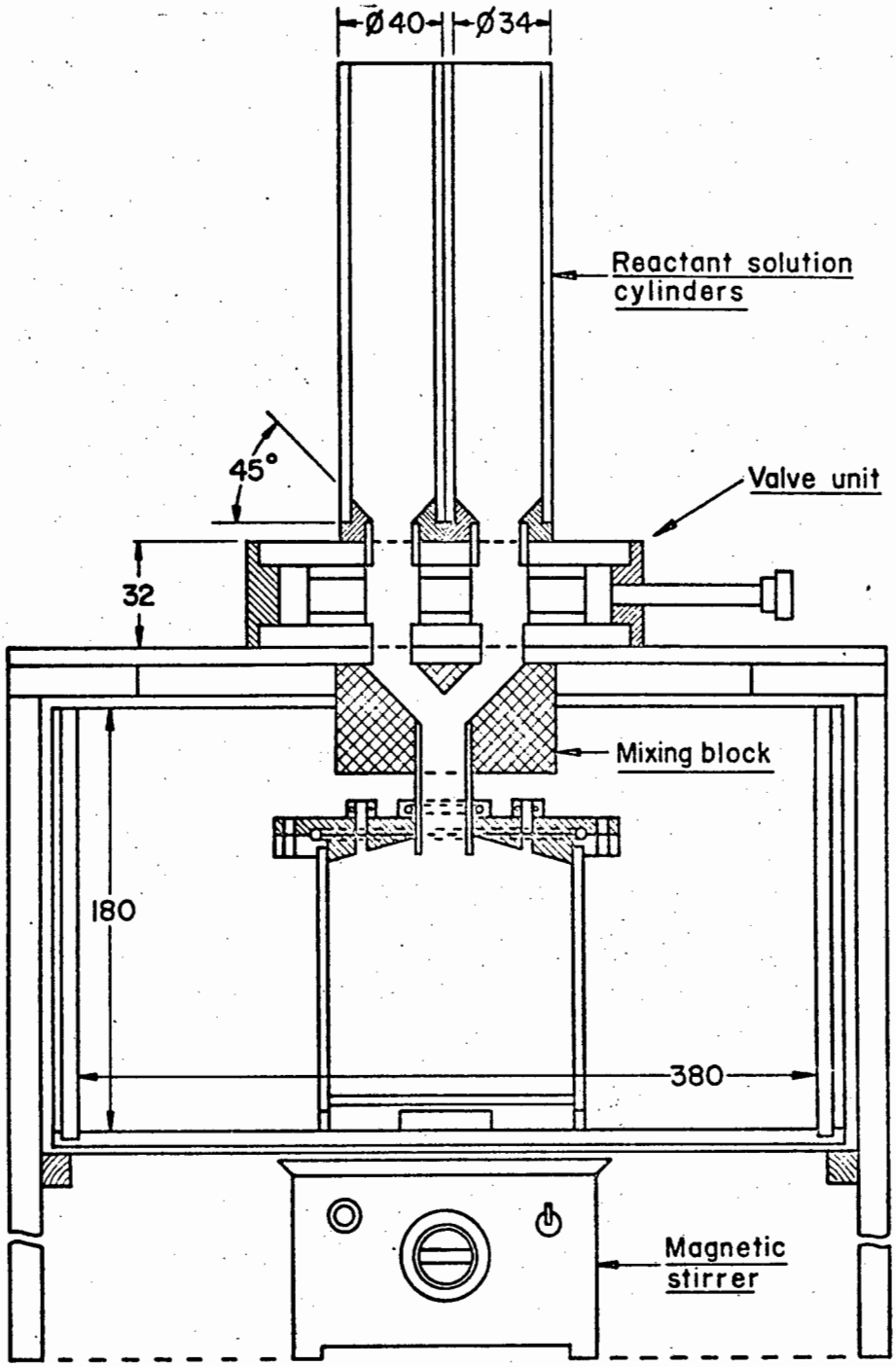

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Figure 3.1. Front elevation of water bath, supporting frame and reactor vessel

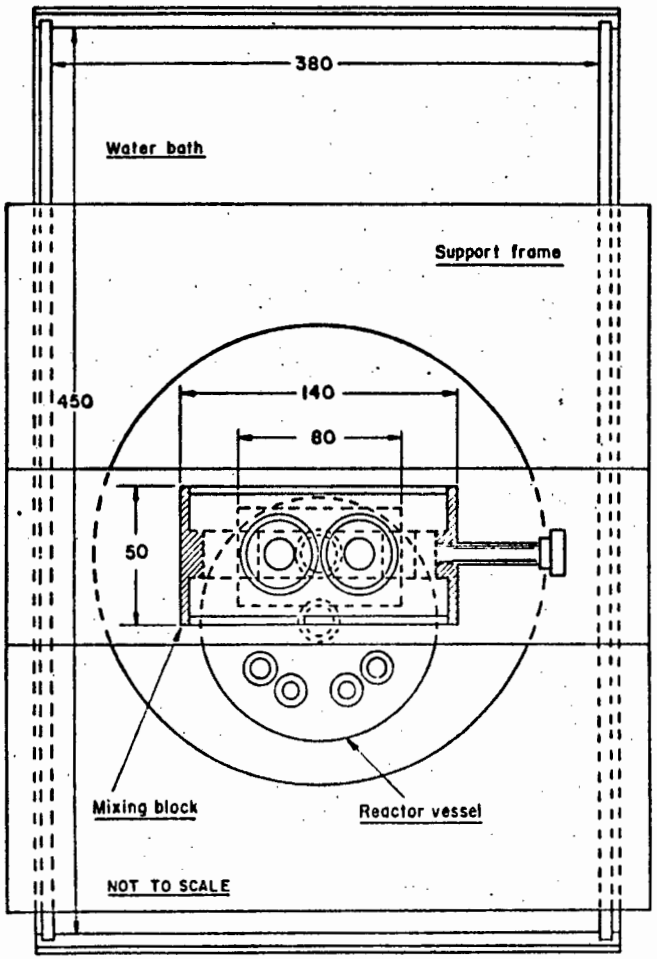

Figure 3.2. Plan of water bath, supporting frame and reaction vessel

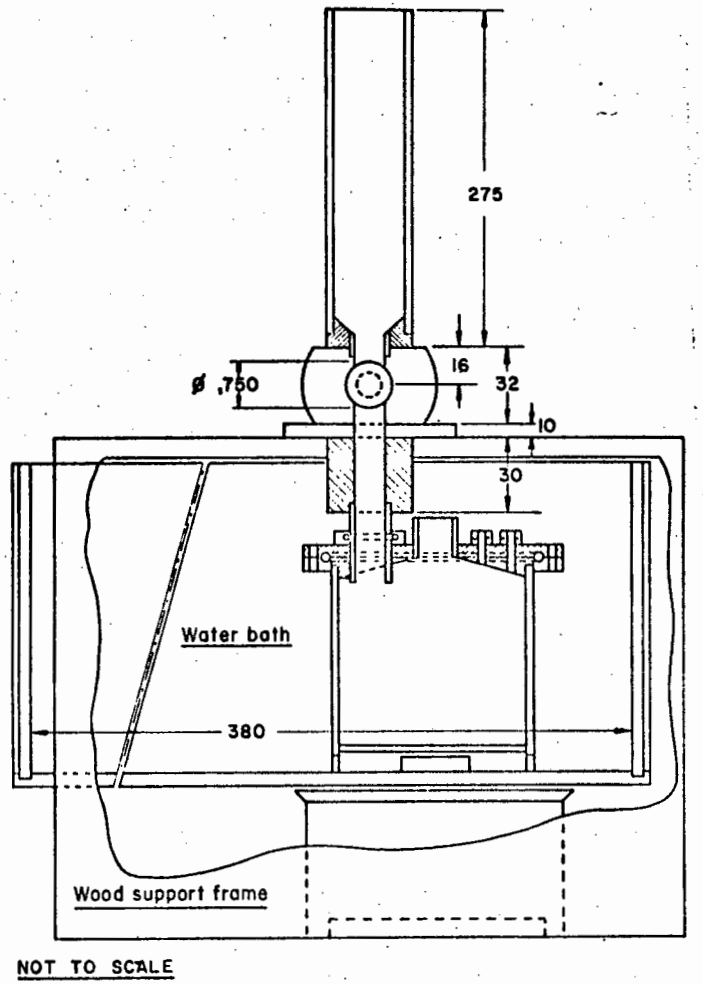

Figure 3.3. Side elevation of water bath, supporting frame and reaction vessel

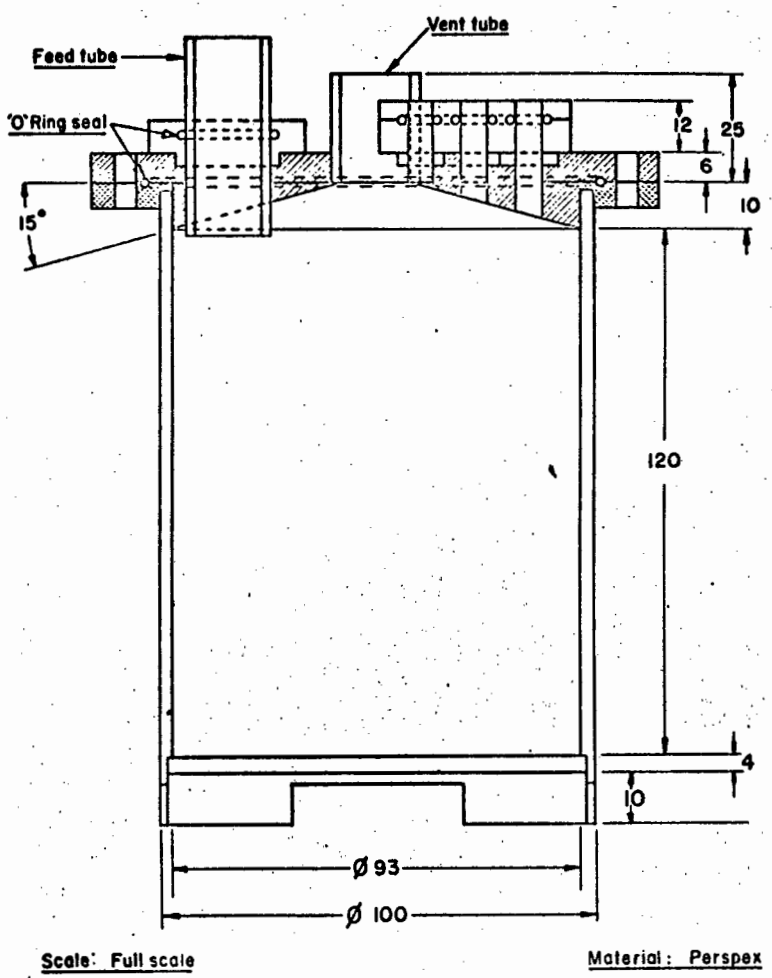

Figure 3.4. Elevation of reaction vessel

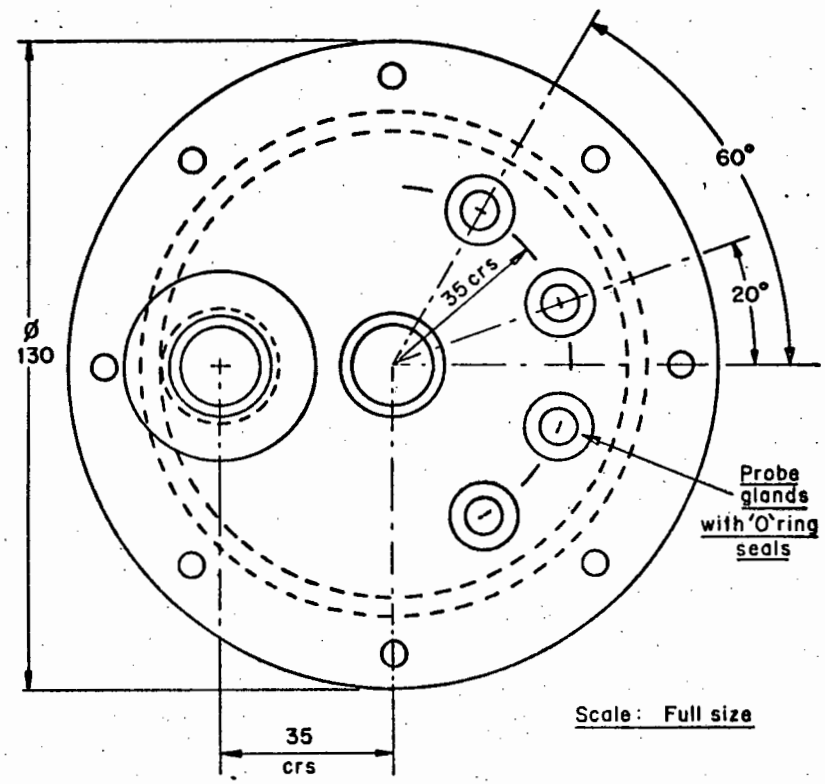

Figure 3.5. Plan of reaction vessel

The reactor stands in a water bath in which the temperature is controlled within ± 0,01°C (HAAKE E52 thermostat). All the reactants and buffers are stored in the water bath to maintain a constant temperature before use. The perspex cylinders are heated by a heating coil to within ± 0,1°C of the required temperature. The reaction solution is stirred by magnetic stirrer, using a Teflon-coated stirring bar. The speed of stirring is usually kept constant.

Experimental procedure

The reactants were made up in two 250 mℓ volumetric flasks, one containing the $NaHCO_3$-NaOH solution, the other the $CaCl_2$ solution. These were poured into the two reactant solution cylinders and on opening the valve discharged through the mixing block to the reactor where the pH change with time was measured. In later experiments it was found preferable to discharge the solution containing the carbonic species first and subsequently the solution containing the calcium species, Mixing intensity was adequate and the pH was already at a high value when the $CaCl_2$ solution was received.

pH meter

A Radiometer pH meter, Type PHM 26C, was used in these experiments. It has the following specifications which makes it suitable for measuring pH changes which occur as calcium carbonate is precipitated from solution :

Read out :	1,4 pH unit for full scale deflection
Smallest scale div. :	0,01 pH
Repeatibility :	± 0,002 pH
Relative accuracy :	± 0,002 pH at buffer point
	± 0,005 pH sample in the range as buffer
	± 0,007 pH typical with buffer and sample in different ranges
Amplifier Drift :	± 0,002 pH/day non-accumulative
Temperature Compensation :	0 to 100°C

Recorder output : 10 mV/pH

The pH meter has a built-in device to correct for loss of electrode sensitivity. The meter has an iso pH adjustment device with which the electrical zero of the output voltage can be set at any convenient value for recorder purposes.

The glass electrode used in these experiments, G202C, is made of glass which responds very rapidly to pH changes.

NBS - standard buffers

NBS standard buffers, in the pH range of interest, were used to calibrate the electrode system. Borax and phosphate buffer solutions were made up as follows : The borax buffer (0,01 M) was prepared by dissolving 3,91 g borax in fresh carbon dioxide free distilled water and making it up to one litre. The phosphate buffer was prepared by dissolving the following quantities of salts in distilled water and making up to one litre,

$K H_2PO_4$ - 3,44 g

Na_2HPO_4 - 3,55 g

The phosphates were dried in an oven at 110°C for 1 to 2 hours and left to cool in a desiccator.

The pH of these NBS standard buffers as a function of temperature has been described by Bates (1954) and is as follows,

Temperature (°C)	20,0	21,0	22,0	23,0	24,0	25,0
Borax pH	9,200	9,210	9,200	9,195	9,185	9,180
Phosphate pH	6,880	6,876	6,872	6,868	6,864	6,860

The accuracy of the pH of these buffers is given as ± 0,01 pH unit.

Strip chart recorder

A Hewlett Packard strip chart recorder type 7100B with amplifier module type 17501A was used in these experiments. It has a chart speed range which covers all the speeds necessary to study the calcium carbonate precipitation reactions. Its specifications are,

Recorder mechanism :	Servo-activated electro-burning pen drive
Response time :	One half second for full scale
Chart speeds :	1;2 inches/hour :
	0,1; 0,2; 0,5; 1;2 inches/minute
	0,1; 0,2; 0,5; 1;2 inches/second

Raw data for the batch tests are recorded in Appendix 2.

3.2 Results and Discussion

Typical results for homogeneous calcium carbonate precipitation experiments are shown in Figure 3.6 where pH is plotted versus time for two different initial reaction conditions. In Figure 3.7 plots are illustrated of the calcium species concentrations, i.e. $[Ca^{2+}]$, $[CaCO_3^o]$ and $[CaCO_3(s)]$ versus time. The values of $[CaHCO_3^+]$ are very low and hence not shown. The concentrations were calculated from the experimentally measured pH values as described earlier.

The calcium species versus time curves (Figure 3.7) can be divided into three distinct regions corresponding to an initial mixing period, an induction period and a precipitation period.

Initial mixing period

The first period corresponds to the initial state of the reaction solution after adding a solution of calcium species at, say pH 7, (made up from $CaCl_2$ stock solution) to a solution of carbonic species at, say pH 10, (made up from $NaHCO_3$ and NaOH stock solutions). On mixing the two solution components the pH of the resultant solution immediately (within two seconds) dropped, e.g. from 10,00 to 9,48 for Experiment 14, and remained at this value for two minutes or longer. From dilution considerations only, such a drop in pH should not occur. The instantaneous drop in pH is attributed to the rapid establishment of an ionic equilibrium, with the formation of ion pairs such as $CaCO_3^o$ and $CaHCO_3^+$. The accompanying changes in $[CO_3^{2-}]$, $[HCO_3^-]$, $[H^+]$ and $[OH^-]$ resulted in a change in pH.

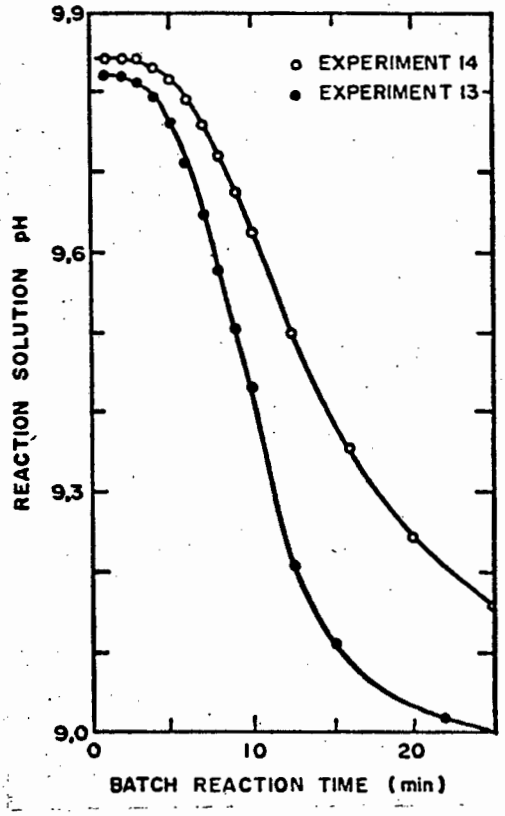

Figure 3.6. Changes in pH with time during homogeneous $CaCO_3$ precipitation

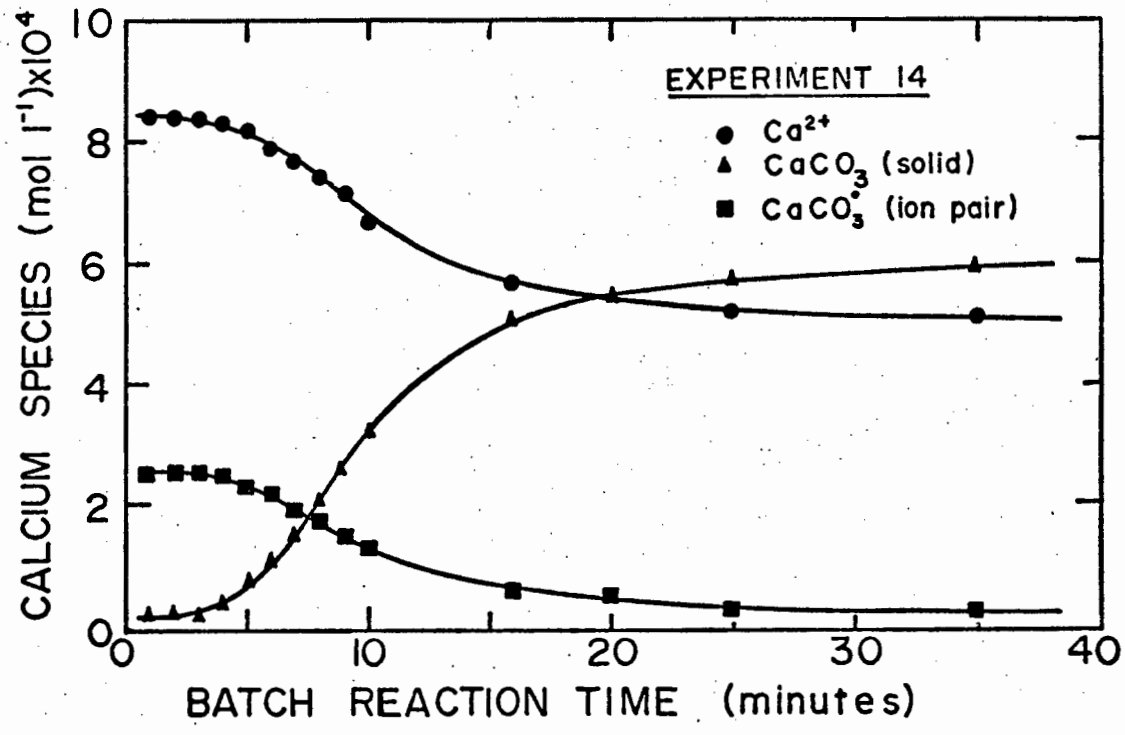

Figure 3.7. Changes in concentrations of solution calcium species with time during homogeneous $CaCO_3$ precipitation

It may be argued that the immediate pH drop is due to rapid $CaCO_3$ precipitation. This consideration can be excluded, since on mixing the two component solutions the resultant solutions remained clear and its pH remained unchanged for several minutes. Furthermore, it can be shown that the pH drop is solely due to ion pairing : From the experimentally determined pH, all the species in solution can be calculated, including the ion pairs $CaCO_3^o$ and $CaHCO_3^+$. The values for the two thermodynamic ion pair dissociation constants, $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$, are calculated from the following relationships,

$$K_{CaCO_3^o} = [Ca^{2+}][CO_3^{2-}].f_D^2/\{[Ca_T^{2+}] + [Ca^{2+}] + [H^+] + [Na^+] - ([OH^-] + 2[CO_3^{2-}] + [HCO_3^-] - [C\ell^-])\} \quad .... \quad (3.29)$$

and

$$K_{CaHCO_3^+} = [Ca^{2+}][HCO_3^-].f_D/\{[OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [C\ell^-] - (2[Ca^{2+}] + [H^+] + [Na^+])\} \quad .... \quad (3.30)$$

Derivations of Equations (3.29 and 3.30) are given in Appendix 3.

By assuming values for $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$, from the literature, and using the known chemical composition of the solution and its experimentally measured pH, all the chemical species concentrations in solution can be calculated (see Appendix 3). The appropriate species concentrations and the $[H^+]$ value (from the pH measurement) are substituted in Equations (3.29 and 3.30) and the calculated K-values are compared with assumed values. Adjustments are made to the assumed values until the calculated values are equal to the

assumed values to within 0,2 percent (see Appendix 3 for computer listing).

Values for $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$ calculated in this fashion were determined for three different Ca_T and C_T values. The calculated K-values are listed in Table 3.1. They are in good agreement with values reported in the literature, also listed in Table 3.1.

Induction period

Ion pair formation is followed by a period of induction. Figure 3.8 shows that the induction period decreases with increasing calcium and carbonate ion concentrations, i.e. increasing oversaturation, where oversaturation is defined as,

$$\Delta[Ca_T] = [Ca_T^{2+}] - [Ca_T^{2+}]_\infty$$

Where $[Ca_T^{2+}]$ = residual total dissolved calcium concentration at time t = t

$[Ca_T^{2+}]_\infty$ = residual total dissolved calcium concentration at time t = infinity

However, even at relatively high degrees of oversaturation (120mg ℓ^{-1} as $CaCO_3$) the induction period is still significant (120 seconds).

Precipitation period

The induction period is followed by a period of rapid precipitation, as shown in Figure 3.8. No attempt was made to fit the results to the rate equation proposed by Reddy and Nancollas (1971) for $CaCO_3$ crystal growth, since the area term in their equation (Eq. 3.28) is ill-defined for a homogeneous precipitation system.

3.3 Conclusions

(1) The almost instantaneous pH drop on mixing the carbonate and calcium solutions indicates that ion pairing reactions are very rapid. This observation is of importance since in all the calculational procedures used to determine species concentrations from measured pH values, it is assumed that the ionic reactions,

Table 3.1

Experimentally derived and literature values for thermodynamic dissociation constants $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$ (at 20,0°C).

EXP	$[Ca_T^{2+}]$	$[C_T]$	$K_{CaCO_3^o}$	$K_{CaHCO_3^+}$
	(mol ℓ^{-1})	(mol ℓ^{-1})	(mol ℓ^{-1})	(mol ℓ^{-1})
13	$1{,}41 \times 10^{-3}$	$2{,}10 \times 10^{-3}$	$(5{,}99 \pm 0{,}70) \times 10^{-4}$	$(5{,}33 \pm 0{,}04) \times 10^{-2}$
14	$1{,}12 \times 10^{-3}$	$1{,}60 \times 10^{-3}$	$(5{,}55 \pm 0{,}69) \times 10^{-4}$	$(5{,}55 \pm 0{,}24) \times 10^{-2}$
15	$0{,}94 \times 10^{-3}$	$1{,}40 \times 10^{-3}$	$(5{,}06 \pm 0{,}68) \times 10^{-4}$	$(5{,}12 \pm 0{,}09) \times 10^{-2}$
Average	-	-	$(5{,}53 \pm 0{,}70) \times 10^{-4}$	$(5{,}33 \pm 0{,}20) \times 10^{-2}$
Garrels and Christ (1965)			$6{,}31 \times 10^{-4}$	$5{,}5 \times 10^{-2}$
Nakayama (1968)			$3{,}29 \times 10^{-5}$	$5{,}64 \times 10^{-2}$
Greenwald (1941)			$1{,}00 \times 10^{-3}$	$5{,}64 \times 10^{-2}$

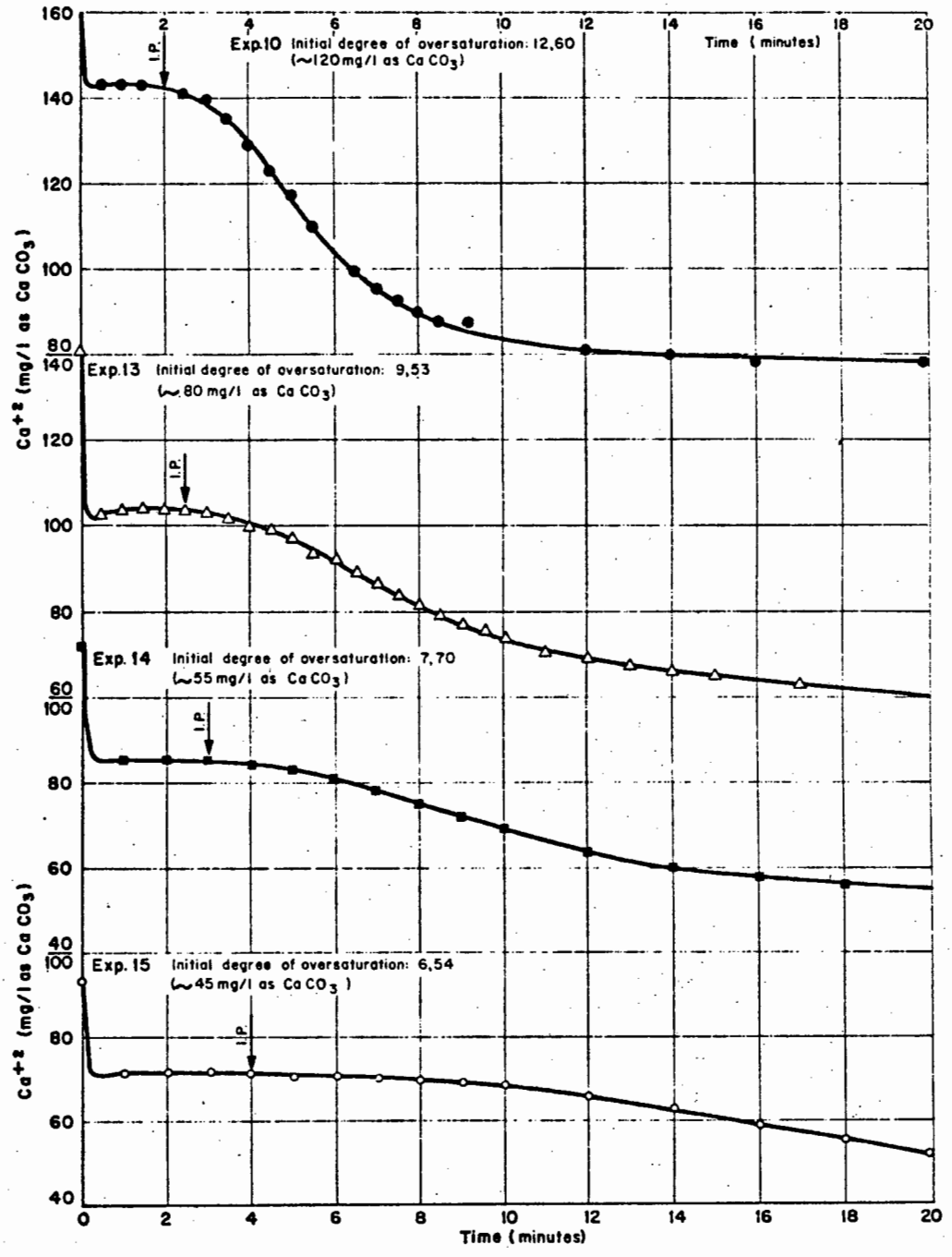

Figure 3.8. The effect of initial degree of oversaturation on the induction period during homogeneous $CaCO_3$ precipitation

including ion pairing, are instantaneous. The above reported experimental results support this assumption.

(2) Although perhaps of limited practical importance, the presence of an induction period before $CaCO_3$ precipitation commences in homogeneous solutions indicates that plug flow reactors without sludge recycling should not be utilized in a recarbonation-softening process. Completely stirred tank reactors (CSTR), even without sludge recycling, should in time develop sufficient crystal seed to eliminate the induction period (see next section).

(3) Since it was evident that batch reactors without sludge inoculation did not appear to have any practical application, no further attempt was made to model $CaCO_3$ precipitation for such systems.

4. HOMOGENEOUS $CaCO_3$ PRECIPITATION IN CSTR SYSTEMS

The batch tests on pure systems demonstrated that the phenomena of ion pairing and induction period are manifested during homogeneous precipitation. In practice, use is often made of the induction period in the single stage stabilization process of potable water in normal water works. The pH of the water is raised to some high value, say 10 to 11, by addition of $Ca(OH)_2$. After removing the precipitate formed on lime addition the clarified water is recarbonated by the addition of carbon dioxide to some pH value near 8 to 9, such that it is in a saturated or slightly supersaturated condition. An intermediate reaction is the formation of carbonate ions, which during recarbonation could theoretically precipitate as $CaCO_3$. However, due to the induction period no precipitation takes place during the short transient period (when the pH is falling) when carbonate ions first form and are then converted to bicarbonate ions. The intermediate states described above may be calculated from a Modified Caldwell-Lawrence Conditioning Diagram (Loewenthal and Marais, 1976).

In the two stage recarbonation-stabilization process the following sequence is followed : In the first stage lime-treated water is contacted with carbon dioxide to react all the hydroxide ions to form carbonate ions (by reducing the pH from say 11,4 to 10,2). The carbonate ions in turn react with the calcium ions to precipitate as $CaCO_3$. This precipitated $CaCO_3$ is removed from the effluent by sedimentation. In the second stage the softened water is stabilized by converting the residual unreacted carbonate ions to bicarbonate ions, by further addition of carbon dioxide (usually entailing a pH drop from 10,0 to 8,4). Induction periods play no role in this two stage recarbonation process. In the first stage the induction period is overcome by using a CSTR system which produces and propagates seed mass, hence precipitation takes place through the mechanism of crystal growth rather than nucleation. In the second stage the softened and often still supersaturated water from the first stage is saturated with respect to $CaCO_3$ by the addition of carbon dioxide.

4.1 Materials and Methods

Pure system unseeded $CaCO_3$ precipitation in CSTR systems was studied for reaction mixtures of $CaCl_2$, $NaHCO_3$ and NaOH simulating lime-treated Pretoria Sewage Works secondary effluent at pH values of 9,4; 9,9; 10,0; 10,7; and 11,3. The simulation related only to the calcium and carbonic species, pH and temperature.

Analytical reagent grade chemicals and demineralized tap water with a conductivity less than 5 µS were used throughout. The reagent solutions (2x220 ℓ) of calcium ($CaCl_2$) and carbonate ($NaHCO_3$ and NaOH) ions were made up to preselected concentrations. Actual concentrations were determined analytically just prior to the commencement of each series of tests.

The reagent solutions were pumped through two calibrated flow meters, a mixing block and finally discharged into a CSTR (Figure 3.9). Both flow rate and reactor volume could be varied to effect eight different residence times, ranging from approximately one to fourteen minutes (Table 3.2). Both hydraulic and average mean residence times are listed. The Hydraulic Residence Time (HRT) was calculated as follows :

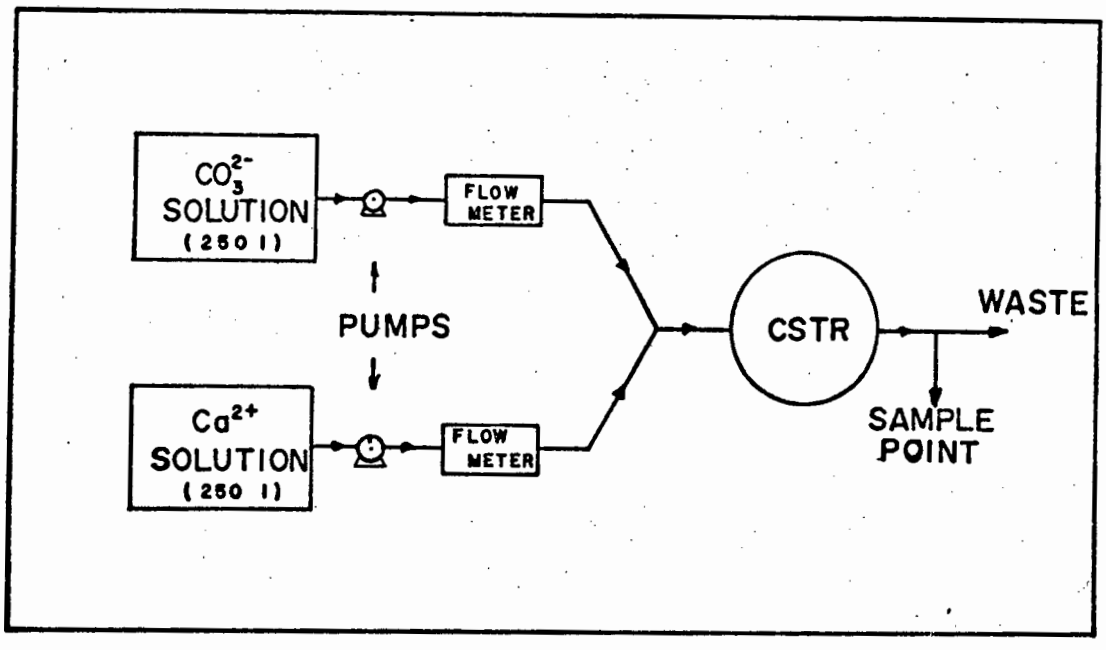

Figure 3.9 Schematic flow diagram of equipment sequence used for bench-scale CSTR studies

Table 3.2

CSTR's residence times for various flow rates

REACTOR IDENTIFICATION CODE	TOTAL FLOW RATE	HYDRAULIC RESIDENCE TIME (HRT)	AVERAGE MEAN RESIDENCE TIME (AMRT)
	$\ell\ min^{-1}$	min	min
2	2,0	0,98	1,07
2	1,5	1,30	1,40
2	1,0	1,95	1,85
2	0,5	3,91	3,42
1	2,0	3,84	3,56
1	1,5	5,13	5,17
1	1,0	7,69	7,45
1	0,5	15,38	14,00

$$HRT = \frac{\text{Reactor Volume } (\ell)}{\text{Total flow rate } (\ell \text{ min}^{-1})} \quad \ldots\ldots \quad (3.32)$$

The true Average Mean Residence Time (AMRT) of effluent flowing through the CSTR was determined by using KCℓ as a tracer in demineralized water (see Appendix 5). The HRT and AMRT in fact were in good agreement, indicating that the mixing in these reactors was very efficient.

The reactor design is illustrated in Figures 3.10 and 3.11 (elevation and plan). Two reactors were used in these studies (see Appendix 5 for details on their dimensions). The reactors were constructed from perspex, allowing visual observation of precipitation and scale formation. Reactant mixture entry was at the bottom of the reactor, underneath the impeller to ensure rapid mixing of the entering stream throughout the reactor. Effluent draw-off from the reactor was over a surface weir. The perspex impeller was driven by an electric motor at approximately 60 rpm. The reactors were baffled with four vertical baffles to ensure efficient mixing. Covers were fixed over the reactors to minimize air solution contact. The covers had three openings, two for pH electrodes (glass and calomel) and one for pressure equalization.

The CSTR tests were conducted at 20°C in a constant temperature room. A test was commenced by switching on the stirrers in the reagent solution tanks to affect thorough mixing (10 minutes). The two reagent solution pumps were switched on and the individual flows were stabilized by adjusting the needle valves on the flow meters. The reactor stirrer was switched on to effect good mixing within the reactor. The reactor effluent was run to waste. After approximately one hour operation under stabilized conditions, samples were taken and analysed. After one to four residence times a second set of samples was taken and analysed. If the analyses of these two sets did not agree to within approximately 5 percent a third set of samples was taken. The flow rate or reactor was then changed to effect a different residence time. Conditions were allowed to stabilize and after an additional three residence times the above sampling procedure

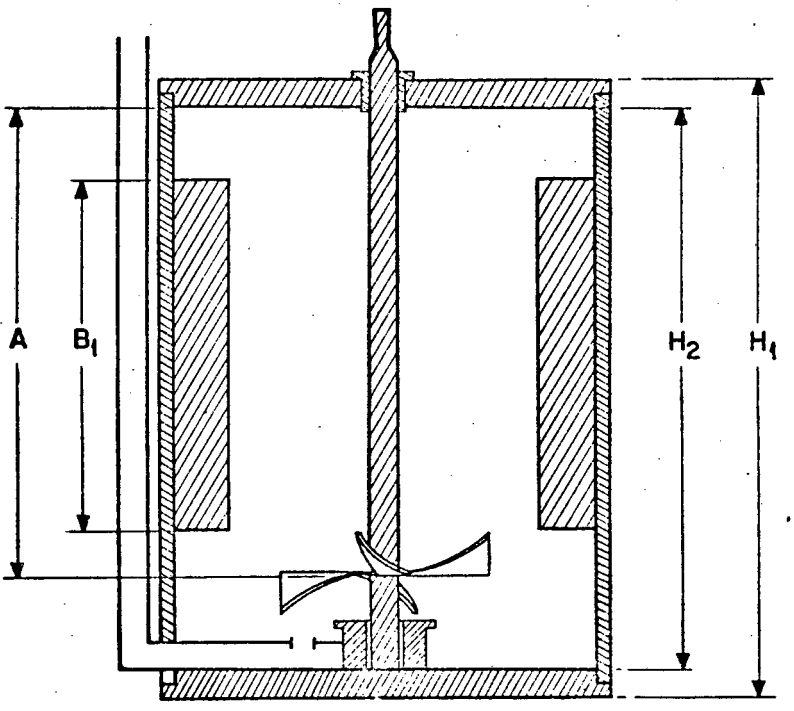

Figure 3.10. Elevation of CSTR

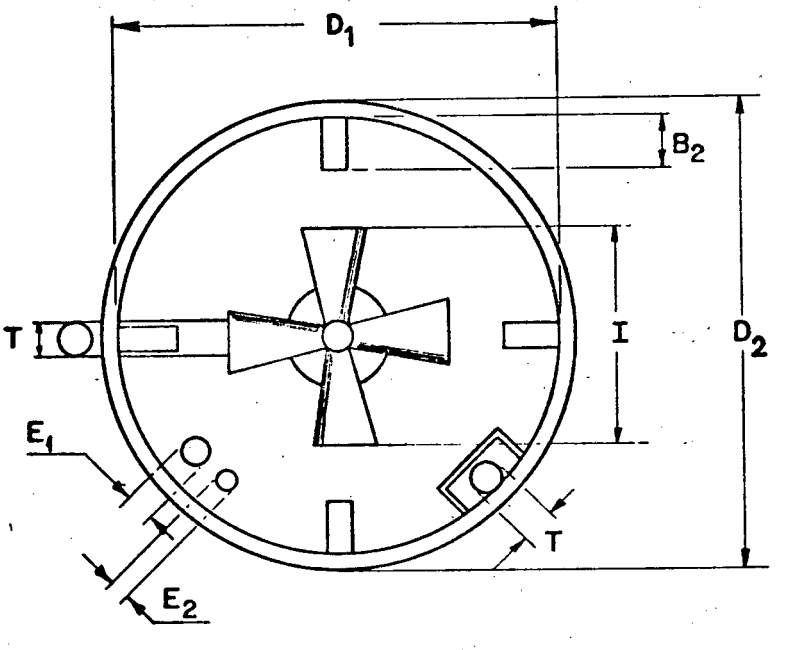

Figure 3.11. Plan of CSTR

was repeated. Precipitation at eight different residence times was studied in this manner.

Samples of effluent were drawn from the effluent stream at the point of discharge from the reactor. Two samples were taken. The first was a sample of reactor effluent with no sample pretreatment. Its pH was determined and it was subsequently acidified with a few drops of a 1:1 $HC\ell:H_2O$ solution to a pH of 2 to 4 and vacuum filtered (to removed acid insolubles) before the determination of total calcium on the filtrate. The second sample was vacuum filtered continuously as it was withdrawn from the reactor, to remove precipitated calcium carbonate. pH, alkalinity and calcium were determined on the filtrate as follows : pH by means of a Radiometer pH meter (Type 29) using a combined glass and calomel electrode; Alkalinity by titration with 0,02N H_2SO_4 to pH 4,2, and calcium by EDTA titration.

Raw data collected for the homogeneous $CaCO_3$ precipitation in CSTR's are listed in Appendix 6.

4.2 Results and Discussion

Starting up

When a continuous run was started up the reaction of the calcium with the carbonate reagent solution resulted in a clear mixture. The reaction mixture remained clear for approximately 5 to 15 minutes, after which it became very turbid. After a further 10 to 30 minutes the reaction solution cleared somewhat to a light milky white appearance and scale build-up on the reactor wall was noted. These observations correspond to various distinct steps in the crystallization process. To initiate the crystallization process an induction period for nucleation was necessary. This was followed by nuclei growth in the bulk of the solution. Simultaneously, epitaxial growth took place on the reactor walls. Finally, conditions stabilized and a steady state was established with nucleation and growth, both in the bulk of the solution and on the reactor walls, taking place at constant rates. The effluent produced under these stabilized conditions was a turbid milky

white solution. Even after standing for periods of an hour or longer, the samples remained turbid, indicating that this effluent was difficult to clarify.

Scale formation

Substantial quantities of calcium carbonate scale formed on the reactor walls during the relatively short (± 4 hrs per reactor) continuous precipitation runs. The scale was a loosely adherent deposit. For one experiment, conducted at a pH of approximately 10,0, the scale formed on the reactor wall was subsequently analysed and identified by X-ray techniques as a mixture of approximately 90 percent calcite and 10 percent vaterite.

To evaluate the mass of scale formed in the reactor a mass balance for calcium was performed over the reactor at various intervals after starting a test-run. In Figure 3.12 the fraction of $CaCO_3$ accumulated in the reactor is plotted as a function of test-run time. This fraction increases with increasing test-run time, but stabilizes after approximately one to two hours. The scaling characteristics of the two reactors differ, probably due to their different hydrodynamic characteristics. The surface to volume ratios of the two reactors are given in Figure 3.12. For identical volumetric flow, more surface area is available in reactor No. 2 than in No. 1. This explains the higher fraction of $CaCO_3$ accumulated in reactor No. 2 as compared to No. 1. The relationship between reactor radius and height for minimum area is,

$$\text{radius}(r) = \text{height}\ (h) \qquad \ldots\ (3.33)$$

(For the mathematical proof, see Appendix 7.)

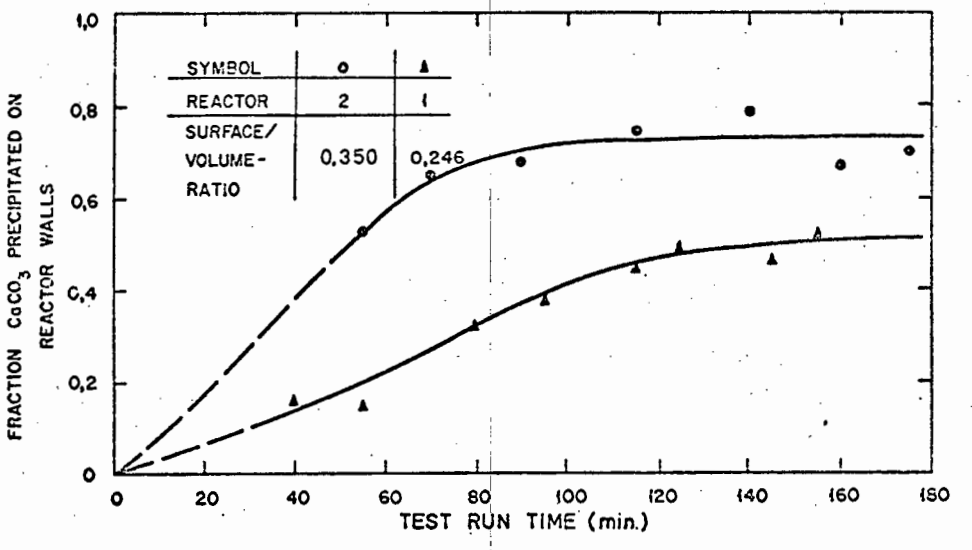

Figure 3.12. $CaCO_3$ scale formation on CSTR walls

A considerable scale build-up was also noted in the PVC tubing joining the reagent mixing block and the reactor. Scale build-up was also noted when static mixers were used, in addition to the mixing block, which resulted in considerable flow reductions. For this reason all the pure system precipitation tests were conducted without static mixers. To ensure comparable conditions for all the experiments, both reactors and the PVC tubing were acid cleaned with a 1:1 $HC\ell:H_2O$ solution before each test run. In addition, samples of reactor effluent were only taken after sufficient time had been allowed for steady state to establish, i.e. one to two hours after starting-up.

The observations regarding serious scale formation during homogeneous calcium carbonate precipitation are consistant with similar observations by Shierholz (1974) who studied $CaCO_3$ precipitation under conditions simulating the lime-soda softening process. This author

Table 3.3

CSTR pure synthetic system $CaCO_3$ precipitation

Average Mean Residence Time	Reactor Effluent pH	Filtered Reactor effluent pH	Alkalinity	Calcium Dissolved/Total	
min	-	-	(mg ℓ^{-1}) as $CaCO_3$)	(mg ℓ^{-1} as $CaCO_3$)	
1,07	10,80	10,55	233	182	236
1,07	10,80	10,65	232	170	235
1,40	10,78	10,67	206	149	195
1,40	10,78	10,64	208	146	201
1.85	10,76	10,68	181	112	192
1,85	10,75	10,67	186	121	207
3,42	10,67	10.50	136	107	228
3,42	10,68	10,50	129	117	-
3,56	10,76	10,70	162	109	233
3,56	10,77	10,70	161	110	245
5,17	10,77	10,70	153	101	234
5,17	10,77	10,62	156	104	247
7,45	10,76	10,60	144	88	259
7,45	10,77	10,58	142	89	274
14,00	10,67	10,48	105	82	323
14,00	10,67	10,50	100	78	313

reported that the deposits formed on the reactor walls had to be scraped off at regular intervals (every *five* minutes) to enhance crystal growth in the bulk of the solution and to prevent a build-up of scale on the reactor walls.

Precipitation at different residence times

Typical results for unseeded calcium carbonate precipitation for a range of CSTR retention times are listed in Table 3.3. For complete tabulation of results see Appendix 6. Graphical illustrations of these results are given in Figures 3.13, 3.14 and 3.15. Approximate figures for percentage reaction completed* for various residence times are listed in Table 3.4. The reactions were 50 to 70 percent complete within five minutes and apparently approximately 100 percent complete within fifteen minutes.

Table 3.4

Degree of reaction completion for simulated lime-treated secondary effluent at various CSTR residence times

Average Mean Residence Time (min)	1,1	5,2	15,2
pH range	Degree of Reaction Completion (%)		
9,28 - 9,62	49	69	93
9,82 - 10,00	51	76	95
9,95 - 10,17	62	87	97
10,67 - 10,80	62	89	97
11,26 - 11,34	75	87	97

*100 percent reaction completion is taken as the concentrations achieved after 24 hours batch reaction time.

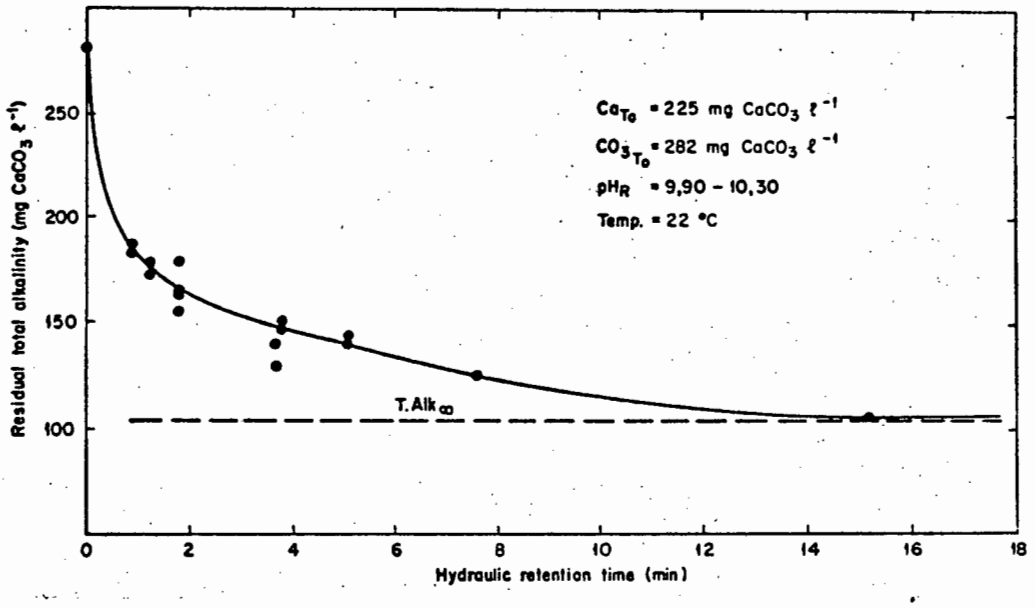

Figure 3.13. Relationship between the residual alkalinity concentration and retention time for continuous unseeded $CaCO_3$ precipitation

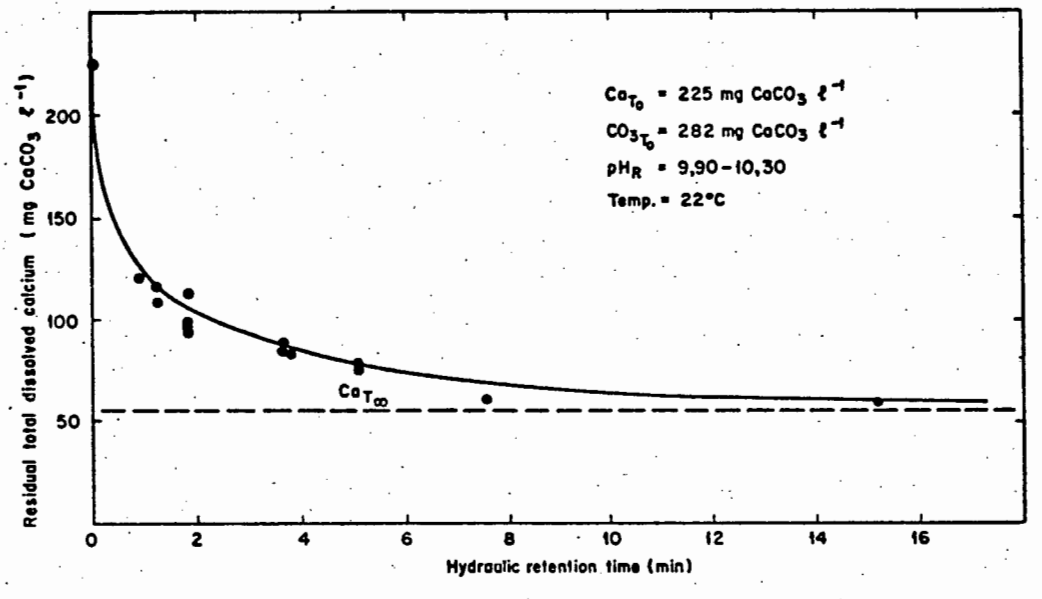

Figure 3.14. Relationship between the residual calcium concentration and retention time for continuous unseeded $CaCO_3$ precipitation

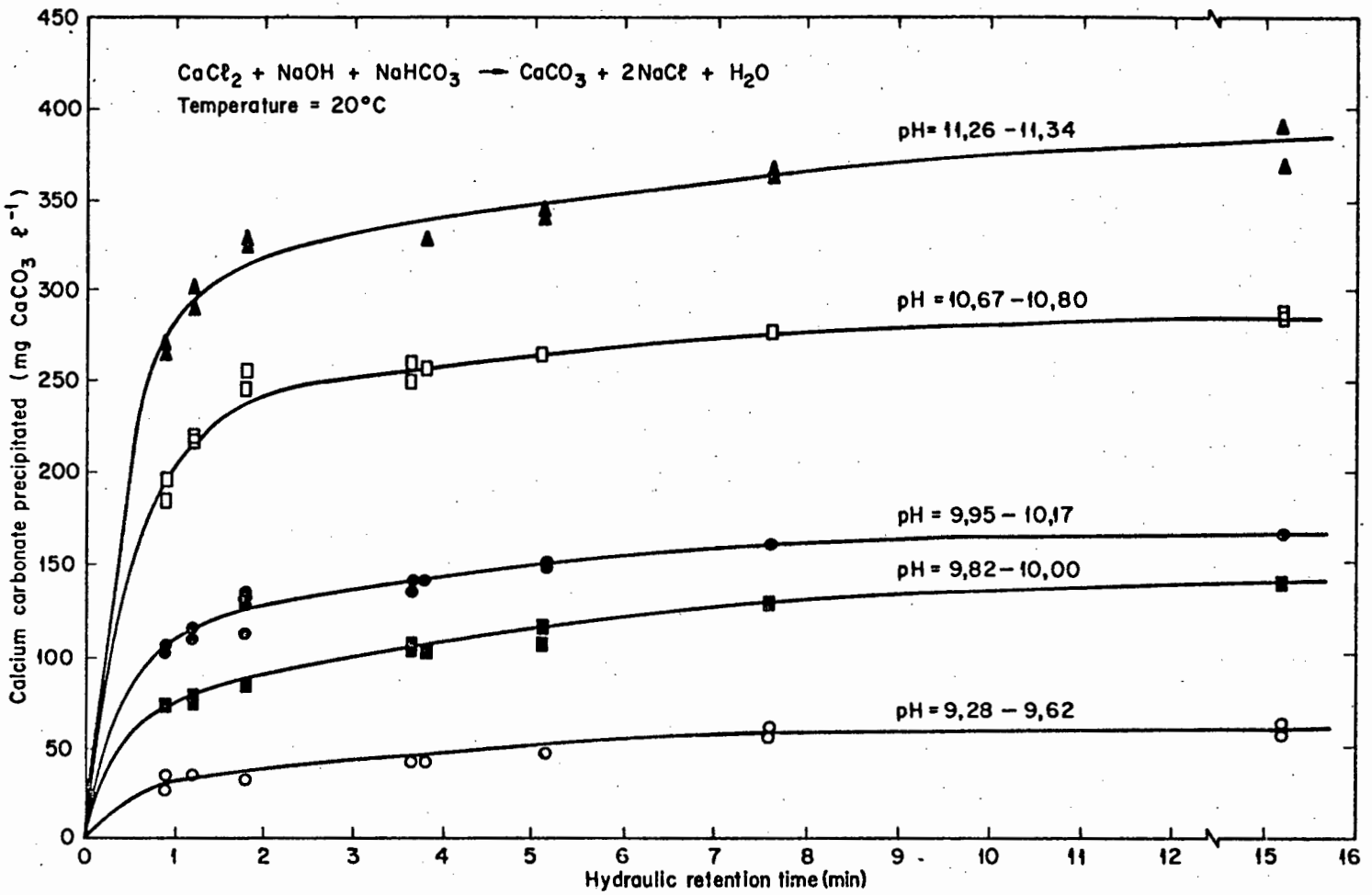

Figure 3.15. Effect of pH and retention time on the mass of $CaCO_3$ precipitated during continuous unseeded $CaCO_3$ precipitation

Rate equation for homogeneous $CaCO_3$ precipitation

It was not possible to establish a rate equation for homogeneous $CaCO_3$ precipitation in the CSTR system because,

(1) Between 40 to 80 percent (see Figure 3.12) of the $CaCO_3$ precipitated from solution accumulated in the CSTR, i.e. crystal growth took place predominantly by the growth of $CaCO_3$ deposits on the reactor wall rather than by crystal growth in the bulk of the solution.

(2) Application of any crystallization model, such as the Reddy and Nancollas rate equation, Eq. (3.28), requires quantitative knowledge of the surface area available for crystallization. In the system under consideration the surface area available for crystallization was ill-defined due to (1) above. In the application of such crystallization models often the surface area is equated to crystal mass, but this assumption only holds for reaction solutions with high crystal seed concentrations, i.e. greater than 400 mg ℓ^{-1} (see Section 5.2).

High pH effluent reaction with carbon dioxide from the air

A problem often associated with alkaline high pH effluents is reaction with carbon dioxide from the air,

$$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O \quad .... \quad (3.34)$$

With subsequent precipitation as calcium carbonate,

$$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3(S) \quad .... \quad (3.35)$$

For this reason the reactors were designed with covers to minimize the problem of effluent-air contact.

It is assumed that the uptake of carbon dioxide is related to the contact time between the effluent and the air, i.e. this phenomenon, if it takes place, will manifest itself at the longer retention times. Carbon dioxide uptake by an effluent does not alter its alkalinity, but it does alter its acidity by an amount equivalent to the mass of carbon dioxide taken up (Loewenthal and Marais, 1976). Table 3.5, lists the total acidity values of various effluents (pH 9,3 to 11,3) for a range of residence times. The results indicate that, with the exception of the very high pH effluents (11,32 at 15,2 minutes), there was no appreciable increase in total acidity with increasing reaction time. It is therefore concluded that carbon dioxide uptake for this particular series of experiments for CSTRs with covers was negligible.

4.3 Conclusions

Homogeneous calcium carbonate precipitation in CSTR systems gave rise to severe scale formation. Scale formed on the reactor walls, stirrer impeller, PVC connecting tubing and static mixers. Scale build-up on the static mixers was so severe that the

Table 3.5

Determination of CO_2 absorption through Acidity changes as a function of reaction time

Average Mean Residence Time (min)	1,1	5,2	15,2
pH range	Acidity x 10^3 (mol ℓ^{-1})		
9,28 - 9,62	2,3	2,2	2,2
9,82 - 10,00	1,6	1,6	1,6
9,95 - 10,17	0,80	0,57	0,78
10,67 - 10,80	-0,19	0,22	-0,18
11,26 - 11,32	-1,9	-1,9	-1,6

reactant flow was reduced to unacceptably low levels within a period of one to two hours. For this reason static mixers could not be used in these experiments. Regular acid cleaning of the reaction system was necessary to minimize this problem. The formation of scale appears to be characteristic of solutions reacting without seed addition, i.e. epitaxial growth with subsequent scale growth is promoted and is dominant.

Confirmatory evidence of the problems created by epitaxial growth is to be found on the full-scale Stander Plant recarbonation process. Similar to scaling problems with the static mixer in the laboratory-scale plant, a full-scale plant static mixer, mixing carbon dioxide with high pH effluent, scaled-up within a month to such a degree that the mixer had to be taken out of service for physical and chemical (acid) cleaning.

The severe scaling problems associated with homogeneous precipitation indicated the need for investigating other modes of $CaCO_3$ precipitation, such as heterogeneous $CaCO_3$ precipitation.

5. HETEROGENEOUS $CaCO_3$ PRECIPITATION IN BATCH REACTORS

In the previous section it was shown that batch precipitation from unseeded solutions gives rise to significant induction periods. In contrast, in CSTR systems the induction period becomes insignificant, but a severe problem of scale formation is encountered. These studies indicated that a more favourable mode of $CaCO_3$ precipitation had to be investigated, i.e. heterogeneous $CaCO_3$ precipitation utilizing seed crystals or sludge. Studies reported in the literature have indicated that sludge recirculation to the reaction vessel promotes high precipitation rates, shorter reaction retention times and possibly an effluent which is easier to clarify.

Reddy and Nancollas (1971) proposed the following rate equation for heterogeneous $CaCO_3$ precipitation in batch reactor systems (see Chapter 2, Eq. 2.30),

$$\frac{d[Ca_T^{2+}]}{dt} = k_G.S.\{[Ca^{2+}][CO_3^{2-}] - \frac{K_{SP}}{f_D^2}\} \quad .... \quad (3.36)$$

They investigated the applicability of this equation under conditions of relatively low supersaturation and pH values not much above 9,0. For these conditions the crystallization rates were so low that it was possible to monitor both Ca_T^{2+} (indirectly, by atomic adsorption analysis on filtered samples) and pH during precipitation. From their work there is no surety that the crystallization theory is applicable under conditions of higher supersaturation and higher initial pH values. In addition more information is required on the effects of temperature, crystal seed mass and stirring speed.

The theory used for determining all the species concentrations and the rate of precipitation by measurement of only pH, i.e. without additional Ca_T^{2+} measurement, as set out previously in Sections 2.3 and 2.4, was used throughout this investigation. The advantage of measuring only pH with time is that much more rapid reactions may be studied than was previously possible when Ca_T^{2+} also had to be measured.

No information was available on whether there is equivalence of behaviour under batch and completely mixed precipitation conditions. Therefore both batch and CSTR heterogeneous $CaCO_3$ precipitation were investigated.

5.1 Equipment and Procedures

The apparatus and experimental procedures were the same as those for the batch studies where no seed crystals were added, as described in Section 3.1. In the heterogeneous precipitation experiments the $CaCO_3$ seed crystals were added to the carbonate solution which in turn was added directly to the reactor. The calcium solution was discharged into the reactor via the injector unit (as previously described). In all the tests, except where indicated otherwise, Hopkins

and Williams Analar grade $CaCO_3$ crystals were used from one specific batch bought from a chemical supplier. The making up of chemical reagents and standardization procedures also followed the procedures described for homogeneous precipitation.

Raw data collected for heterogeneous $CaCO_3$ precipitation in batch reactors are listed in Appendix 4.

5.2 Results and Discussion

Typical examples of pH-time curves for calcium carbonate crystallization from solutions are given in Figure 3.16. Knowing the initial reactant concentrations and the observed pH changes with time, the following time dependent parameters were calculated (see Sections 2.3 and 2.4) using the computer program EXPDA1 listed in Appendix 9,

H^+ ; OH^- ; $CaHCO_3^+$; $CaCO_3^o$; $CaCO_3(S)$;

H_2CO_3 ; HCO_3^- ; Ca^{2+}; CO_3^{2-}; f_M and f_D.

Plots of some of the derived values for one of the experiments (Experiment 35H, Appendix 4) are shown in Figure 3.17. To determine the rate constant, k_G, in Eq. (3.36), the derived values Ca^{2+}, CO_3^{2-}, $CaCO_3(s)$ and f_D were plotted according to

$$\Delta[Ca^{2+}]/\Delta t \quad \text{versus} \quad CaCO_3(s).\{[Ca^{2+}][CO_3^{2-}] - K_{sp}/f_D^2\}$$

Theoretically if k_G is constant the data should plot to a straight line passing through the origin, as is evident in Figure 3.18. This proportional linear plot was exhibited in all the heterogeneous $CaCO_3$ precipitation experiments (approximately 100, see Appendix 4). These plots therefore provide support for the crystallization model of Reddy and Nancollas (1971).

Once it was evident that the Reddy and Nancollas model appeared to be applicable, an investigation was instituted to determine the factors influencing the value of k_G. This involved investigation of five aspects, viz. the effects of,

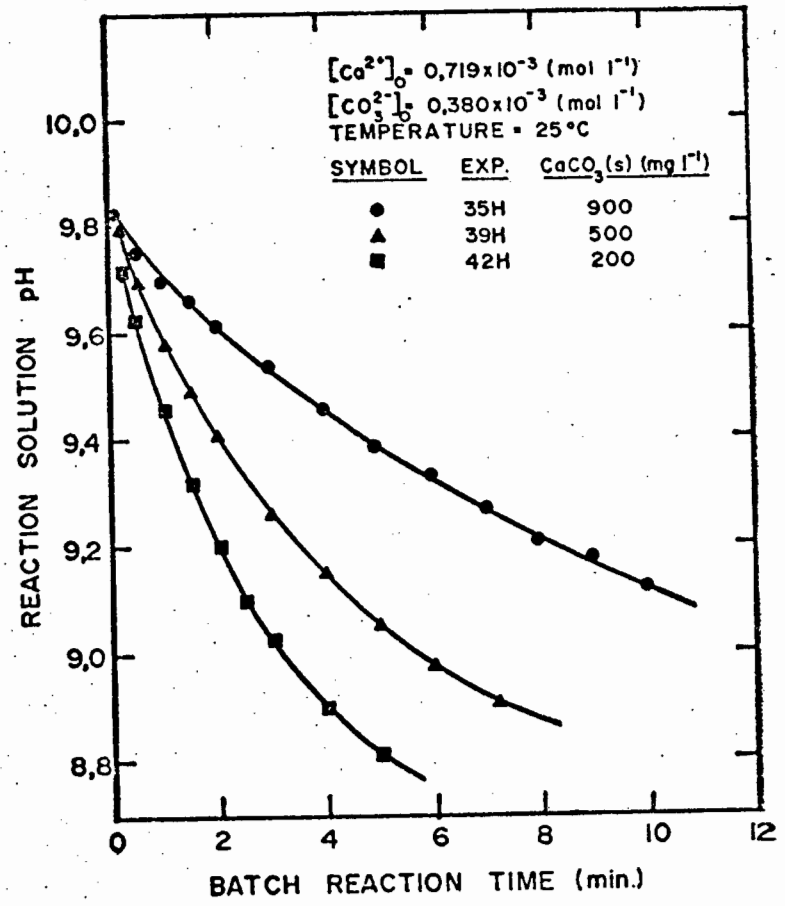

Figure 3.16. The effect of the concentration of inoculated seed mass on heterogeneous $CaCO_3$ precipitation

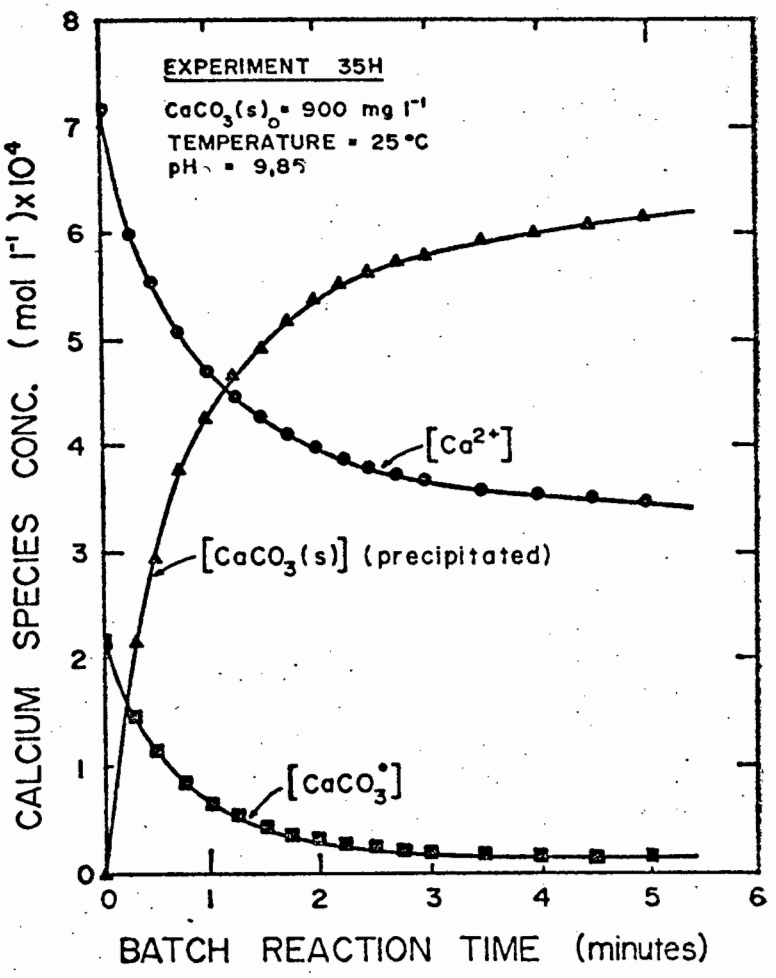

Figure 3.17. Changes in the concentrations of solution calcium species as a function of time during heterogeneous $CaCO_3$ precipitation

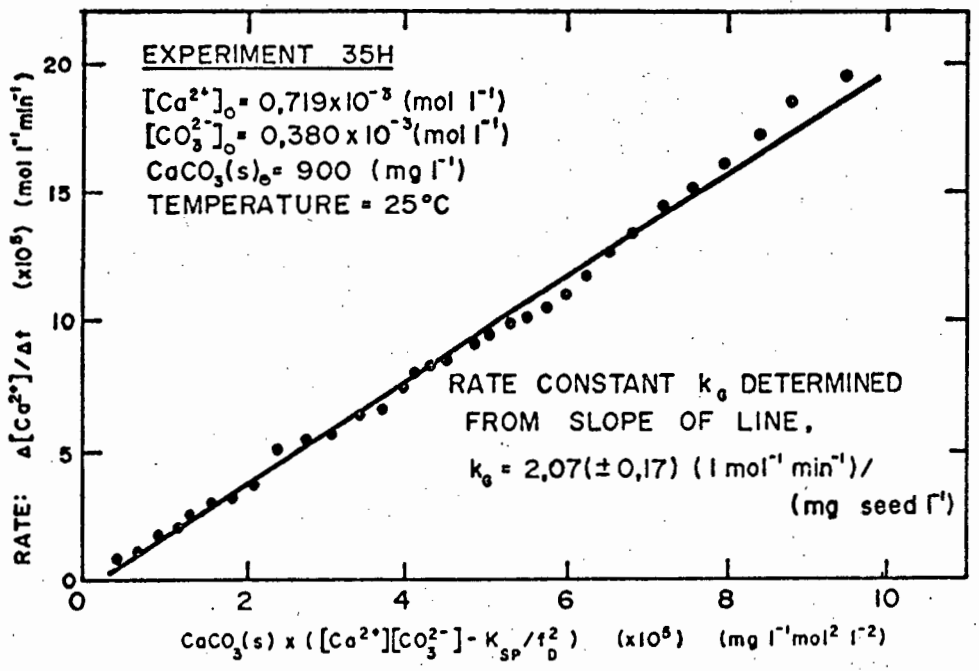

Figure 3.18. Kinetic plot used for determining rate constant k_G for $CaCO_3$ crystal growth

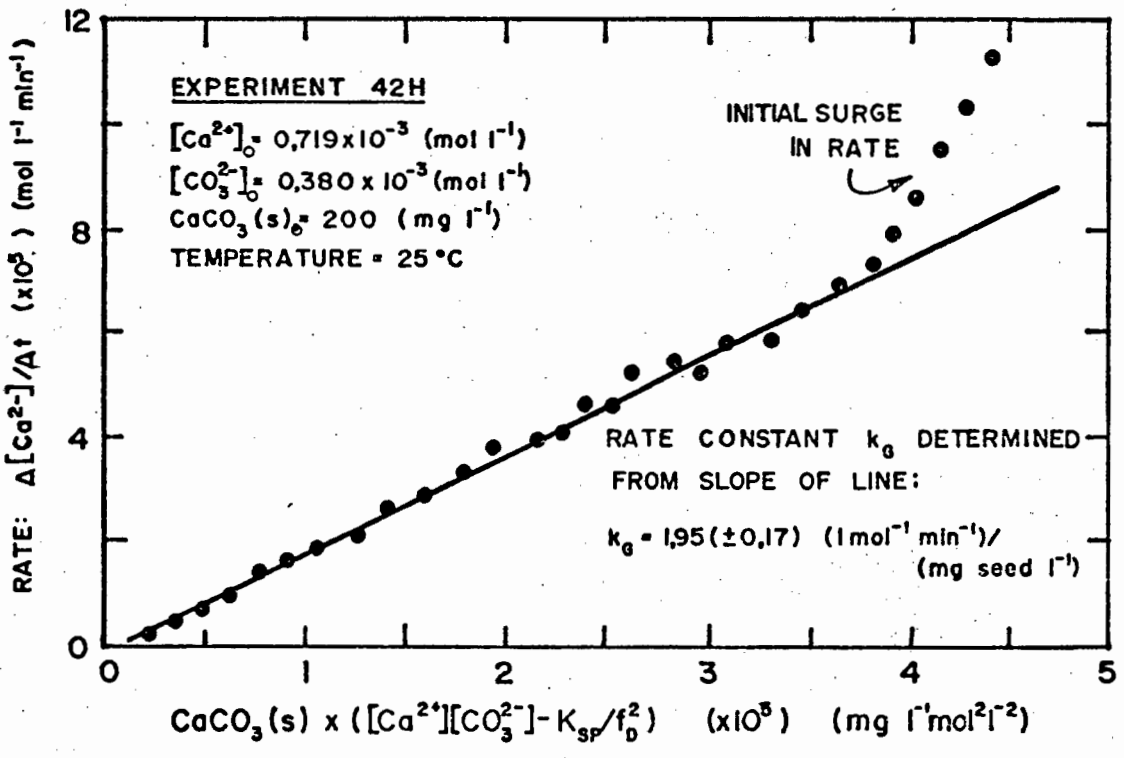

Figure 3.19. Kinetic plot indicating a surge in $CaCO_3$ growth when inoculated seed mass was low

(1) various seed concentrations for constant initial reactant concentrations,
(2) various initial reactant concentrations for constant seed concentration,
(3) seed crystal type,
(4) temperature, and
(5) stirring speed.

Effect of seed concentration

Constant reactant concentrations of Ca^{2+} and CO_3^{2-} of $0,719 \times 10^{-3}$ and $0,380 \times 10^{-3}$ mol ℓ^{-1} respectively, were inoculated with crystal seed masses ranging from 100 to 1000 mg ℓ^{-1}. The stirring speed was kept constant at 500 rpm and the temperature at 25°C. The results are listed in Table 3.6. The value of k_G remained approximately constant over this range of crystal seed concentrations at,

$k_G = 2,1 \pm 0,2$ (ℓ mol^{-1} min^{-1}).(mg seed ℓ^{-1})$^{-1}$

Table 3.6

Rate constant, k_G, for various seed crystal concentrations

Experiment No	Seed crystal concentration (mg ℓ^{-1})	Rate constant k_G (ℓ mol^{-1} min^{-1}). (mg seed ℓ^{-1})$^{-1}$
34H	1000	2,47
35H	900	2,44
36H	800	2,24
37H	700	2,80
38H	600	2,50
39H	500	2,46
40H	400	2,58
41H	300	2,15
42H	200	2,18
43H	100	2,37

$[Ca^{2+}]_o = 0,719 \times 10^{-3}$ mol ℓ^{-1}; $[CO_3^{2-}]_o = 0,380 \times 10^{-3}$ mol ℓ^{-1}; Stirring speed 500 rev.min^{-1}; Temperature = 25°C

At seed crystal concentrations less than 400 mg ℓ^{-1} an initial surge in the growth rate was observed (Figure 3.19) with subsequent time-crystallization behaviour according to Eq. (3.36) and the value of k_G unchanged. The initial growth surge can be attributed to the formation of new nuclei under conditions where insufficient area or growth sites are supplied by the inoculated crystals.

Effect of initial reactant concentrations

In this series of tests the seed crystal mass was kept constant at 700 mg ℓ^{-1} and $CaCl_2$, $NaHCO_3$ and NaOH concentrations were varied over a wide range of molarities, as listed in Table 3.7. Again the stirring speed and temperature were kept constant at 500 rpm and 25°C, respectively. The derived data are also listed in Table 3.7. It is evident that the initial concentration influences the rate constant. It appears that the k_G value can be related to the initial ionic equilibrium pH value, pH_o. A plot of pH_o versus k_G is shown in Figure 3.20 for MERCK, and HOPKINS and WILLIAMS brand crystals.

Considering the series of experiments reported in this and previous subsections it would seem that the value of k_G is dependent only on the *initial* pH value and that in the course of the crystallization experiment this k_G value is unaffected by the reduction in pH (see Figure 3.21). If, in the course of the experiment, the k_G value was influenced by pH then at the same pH the slopes of the experimental plots reported in Figure 3.21 should be the same, whereas this was not observed. No satisfactory hypothesis could be advanced for this observed behaviour. These results cast doubt on the general validity of the Reddy and Nancollas model. (This is dealt with in greater detail on p 142).

Effect of seed crystal type

To investigate the effect of different seed crystal types on the $CaCO_3$ precipitation rate, the set of experiments reported in the previous subsection were repeated using HOPKIN and WILLIAMS brand $CaCO_3$ crystals for seed instead of MERCK brand crystals. The results are shown in

Table 3.7

Rate constant, k_G, for various reactant concentrations and initial pH values

Experiment No	$[CaCl_2]$ x 10^3	$[NaHCO_3]$ x 10^3	$[NaOH]$ x 10^3	$[Ca^{2+}]$ x 10^3	$[CO_3^{2-}]$ x 10^3	pH_o (t = 0)	Rate Constant k_G
40	3,720	3,480	1,310	2,838	0,453	9,51	1,11
41	3,720	3,078	1,210	2,862	0,379	9,52	1,12
43	3,720	2,305	0,906	3,087	0,287	9,50	1,03
44	3,720	1,920	0,756	3,187	0,232	9,49	0,98
45	3,720	1,535	0,605	3,291	0,179	9,47	0,98
46	2,790	3,460	1,320	2,001	0,539	9,59	1,35
47	2,790	3,078	1,210	2,054	0,486	9,64	1,37
48	2,790	2,790	1,060	2,136	0,401	9,64	1,40
49	2,790	2,305	0,906	2,225	0,335	9,63	1,30
50	2,790	1,920	0,756	2,311	0,271	9,57	1,20
54	1,940	2,680	1,060	1,396	0,493	9,69	1,68
55	1,940	2,330	0,906	1,462	0,405	9,67	1,66
56	1,940	1,915	0,756	1,533	0,324	9,65	1,54
57	1,940	1,530	0,605	1,608	0,247	9,63	1,59
62	0,970	9,915	0,756	0,700	0,433	9,78	1,70
63	0,970	1,530	0,605	0,745	0,329	9,77	1,89

Temperature = 25°C; Stirring rate = 500 rev min^{-1}; $CaCO_3$ seed concentration = 700 mg ℓ^{-1};
All concentrations are in mol ℓ^{-1} and rate constant units are (ℓmol^{-1} min^{-1}). (mg seed ℓ^{-1})

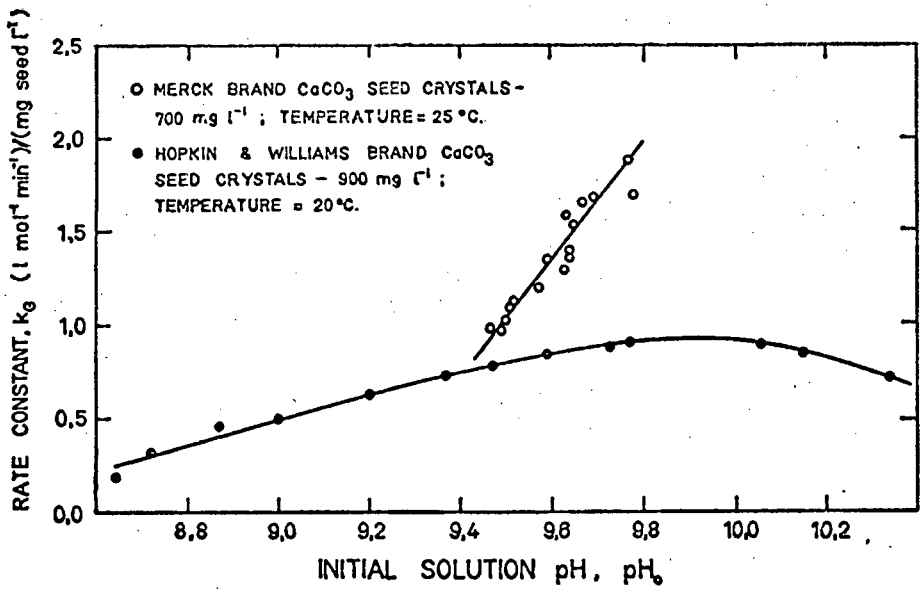

Figure 3.20. Plot indicating apparent relationship between the rate constant (k_G) and initial pH (pH_o) for two brands of $CaCO_3$

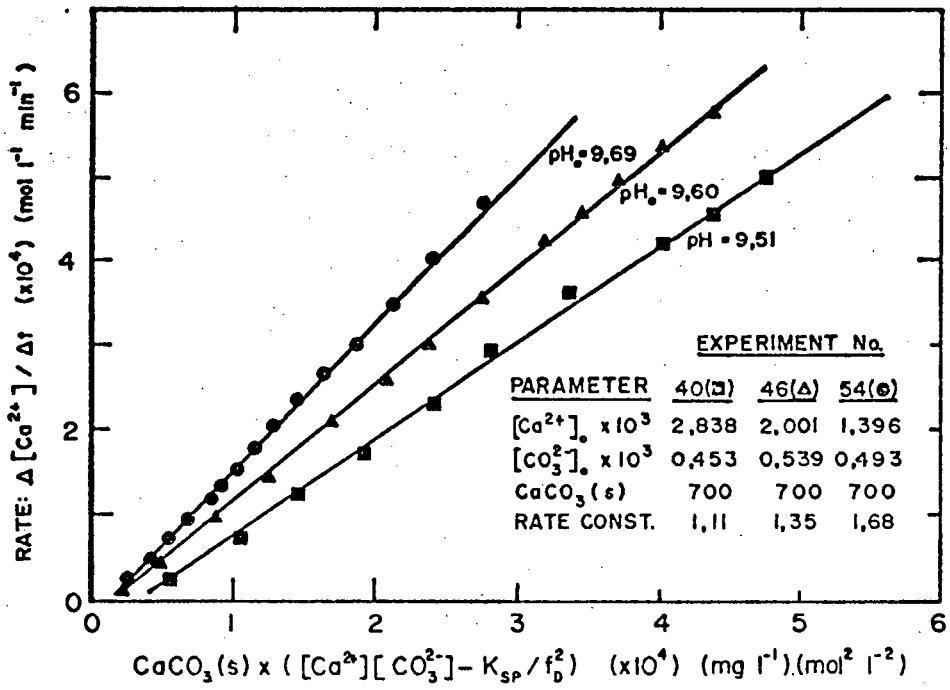

Figure 3.21. Effect of initial pH (pH_o) on rate constant k_G

Figure 3.20. It is evident that the crystal type has a profound effect on the rate constant, possibly because of the different surface area to mass ratio for these two crystal types (see Appendix 18). It is also evident that pH has a significant effect on the k_G value for HOPKIN and WILLIAMS brand $CaCO_3$ crystals.

Subsequently, when this particular batch of HOPKIN and WILLIAMS $CaCO_3$ crystals was used up, another batch of the same manufacturer brand was used, and even here it was evident that the k_G value was different from that observed for the first batch. This was rather unfortunate for it put a limitation on the extent of the investigation possible by using only the first batch.

Effect of Temperature

To study the effect of temperature on k_G the same initial reactant concentrations were used and crystallization was monitored at temperatures 10, 20, 30 and 40°C. At each temperature the seed mass was varied from 400 to 800 mg ℓ^{-1}. The measured variation of k_G with temperature included the effect of pH_o, since pH is also a function of temperature. The results are listed in Table 3.8 and illustrated in Figure 3.22. To determine the functional relationship of k_G with temperature an Arrhenius plot, ln k_G versus 1/T, was made as shown in Figure 3.23. It appears that the Arrhenius equation,

$$\ln k_G = \ln A - E/RT \quad \ldots\ldots \quad (3.37)$$

adequately models the temperature dependence of k_G. The values of ln A and E were determined by applying a linear least squares fit to the data points in Figure 3.23 to give,

Table 3.8

Rate constant, k_G, for $CaCO_3$ precipitation at various temperatures

Experiment No	Crystal seed conc. (mg ℓ^{-1})	Temperature (°C)	Rate Constant k_G
1	400	10,6	0,92
2	500	11,0	0,89
3	600	11,4	0,95
4	700	10,6	0,76
5	800	10,8	0,79
6	400	20,8	1,64
7	500	20,5	1,48
8	600	20,4	1,47
9	700	20,8	1,51
10	800	20,8	1,54
11	400	29,0	2,52
12	500	29,1	2,55
13	600	29,0	2,49
14	700	29,1	2,37
15	800	29,0	2,41
16	400	39,8	4,91
17	500	39,7	4,77
18	600	40,0	4,57
19	700	39,0	3,53
20	800	39,0	4,20

Reactant concentrations (mol ℓ^{-1}): $CaCl_2 = 1,19 \times 10^{-3}$; $NaHCO_3 = 1,56 \times 10^{-3}$; $NaOH = 0,69 \times 10^{-3}$; Stirring speed = 500 rev min^{-1}.

$$\ln A = 18,0 \ (\pm\ 1,5)$$
$$E = 10,3 \ (\pm\ 0,9) \text{ kcal mol}^{-1}$$

An activation energy of this magnitude implies that the reaction is surface controlled. This value of E is in good agreement with that found by Reddy and Nancollas (1971), i.e. E = 11,0 ($\pm$ 1,0) kcal mol^{-1}. Thus, even at the fairly high rates of crystallization observed here

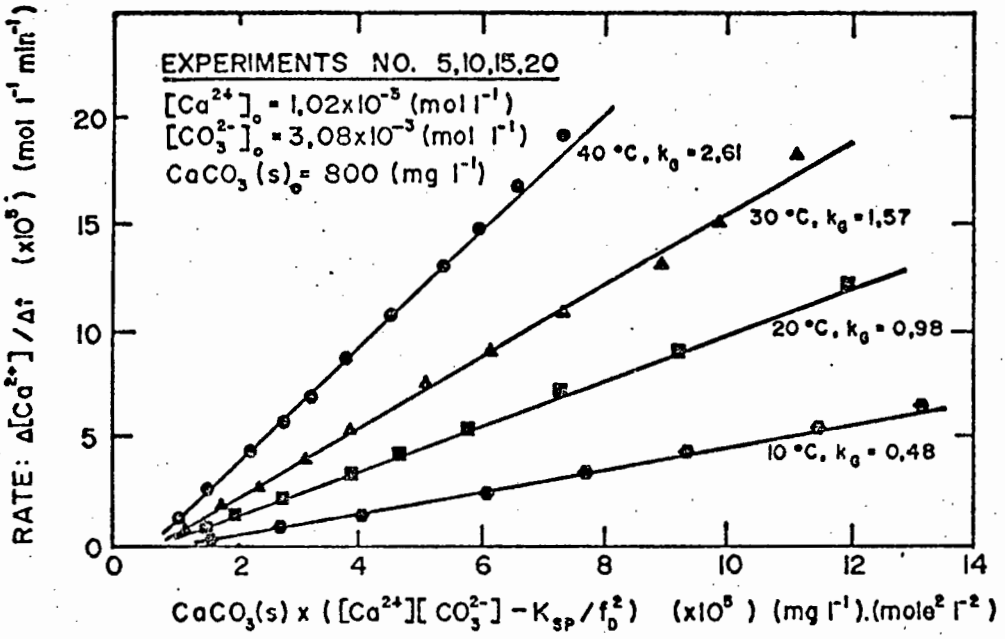

Figure 3.22. Effect of temperature on the rate constant for $CaCO_3$ precipitation

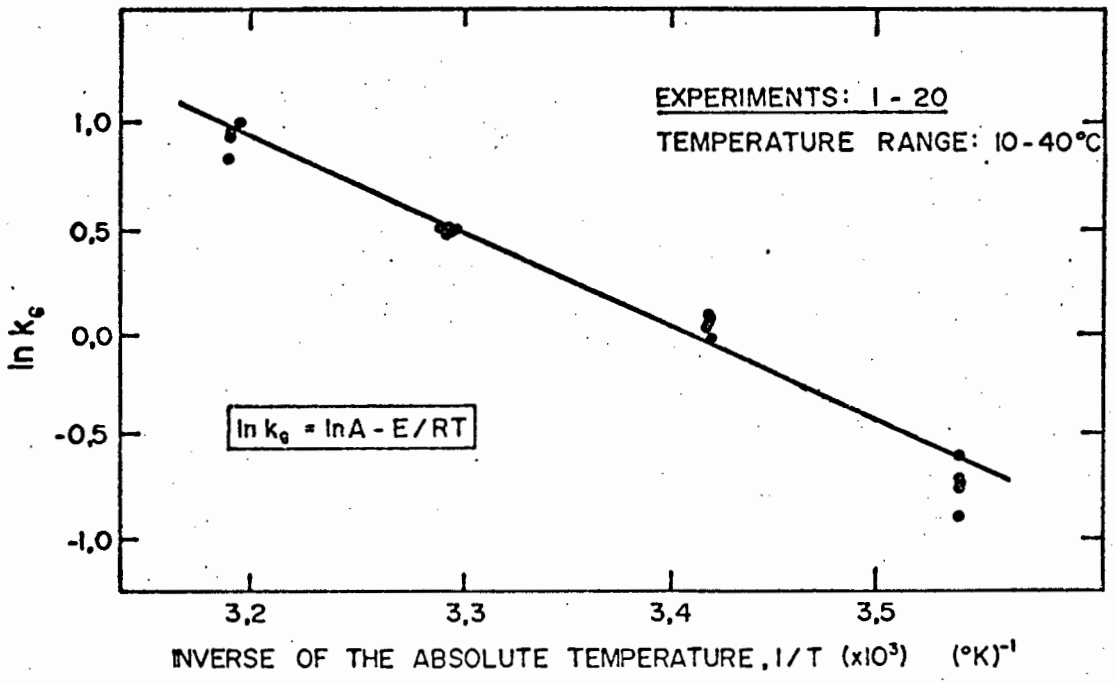

Figure 3.23. Arrhenius plot for heterogeneous $CaCO_3$ precipitation

the crystallization mechanism still appears to be surface controlled.

The Van't Hoff-Arrhenius equation is widely used by engineers to determine temperature effects, i.e.

$$K_T = K_{20}^{\theta(T-20)} \quad .... \quad (3.38)$$

or

$$\log K_T = \log K_{20} + (T-20) \log \theta \quad .... \quad (3.39)$$

where T = temperature in deg C
K_T, K_{20} = K at temperature T^oC, 20^oC, respectively
θ = constant

To determine if the k_G values obtained in this investigation obey Eq. (3.39) a plot was made of log k_G versus temperature (Figure 3.24). The plot approximated to a straight line yielding

$$k_G = 1{,}449 \times (1{,}060)^{(T-20)} \quad .... \quad (3.40)$$

Effect of stirring speed

To determine the effect of the stirring speed on the rate constant, k_G, stirring speeds ranging from 300 to 800 rpm were investigated (see Table 3.9). A minimum stirring speed of 400 rpm was necessary to keep the crystals in suspension in the reactor solution. Stirring speeds higher than this value did not preceptibly change the rate constant. Independence of k_G from the stirring speed lends further support to a surface controlled mechanism for crystallization (Reddy and Nancollas, 1971).

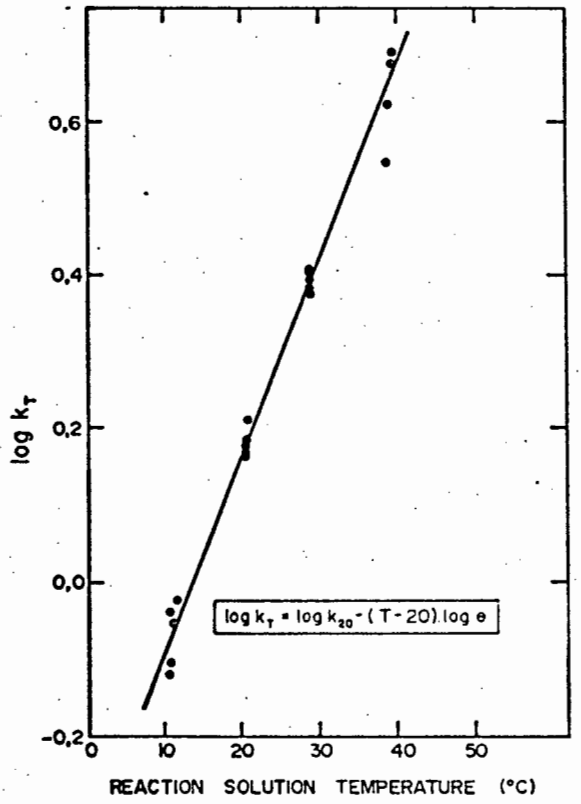

Figure 3.24. Van't Hoff plot for heterogeneous $CaCO_3$ precipitation.

Table 3.9

$CaCO_3$ crystallization rate constant, k_G, for various stirring rates

Experiment No	Stirring rate (rev min^{-1})	Rate constant K (ℓ mol^{-1} min^{-1}). (mg seed ℓ^{-1})$^{-1}$
30	300	1,46
31	400	1,66
32	500	1,82
33	600	1,94
34	700	1,74
35	800	1,86

As indicated in the literature review (Chapter 2, Section 3.4) Eq. (3.36) does not conform to any of the standard forms for precipitation reactions, i.e. Eqs. (2.18, 2.19 and 2.21). It is therefore not possible to conclude from the form of Eq. (3.36), whether $CaCO_3$ crystal growth is surface or diffusion controlled. However, additional data in the form of the magnitude of the activation energy for the reaction and the independence of reaction rate on turbulence, both indicate surface controlled growth. It was decided to retain the form of Eq. (3.36) to test the applicability of the Reddy and Nancollas model for data collected in this study. As demonstrated in the previous five subsections, rate Equation (3.36) was found valid for data collected in this study and hence other models conforming to the standard forms for precipitation kinetics were not pursued. Subsequent to the study reported in this thesis Sturrock, Benjamin, Loewenthal and Marais (1976) (members of the same research team at the University of Cape Town) pursued this matter further, deriving a more satisfactory rate equation of the form,

$$\frac{\delta[CaCO_3]}{\delta t} = k_G.M.f_D^2\{[Ca^{2+}]^{\frac{1}{2}}\ [CO_3^{2-}]^{\frac{1}{2}} - (\frac{K_{sp}}{f_D^2})^{\frac{1}{2}}\}^2 \qquad \ldots\ (3.41)$$

This equation conforms to the general form of the rate equation for surface controlled crystal growth proposed by Davies and Jones (1955). The fact that Reddy and Nancollas (1973) continued to investigate the applicability of Eq. (3.36) when they had knowledge of Eq. (2.21), is indicative of the uncertainty in rate equation formulation common to all kinetic investigations. Sturrock *et al* applied Eq. (3.41) to the data collected in this thesis investigation. They found that the inconsistancy reported above, i.e. the k_G dependence on pH_o, fell away when Eq. (3.41) was used.

From a practical point of view, although Eq. (3.41) has the merit of reflecting an apparently more satisfactory description of the precipitation process, it is a complex relationship which, within a restricted

range of usage, does not really give improved predictions over Eq. (3.36). Sturrock *et al* observed that even with their rate Equation (3.41) the k_G value was still very sensitive to crystal type. The rate may change by as much as a factor of 5 depending on the brand crytal seed utilized. In Chapter 4 it will become evident that the kinetics of the $CaCO_3$ precipitation process are in fact not a crucial factor in the design of water reclamation plants. For these reasons it was adequate to retain Eq. (3.36) as the basic model on which $CaCO_3$ precipitation kinetics could be modelled in this chapter.

5.3 Application

In the batch tests reactant and crystal seed concentrations were known and the pH changes with time were measured. Using this data the change in species concentrations with time and the rate constant, k_G, were calculated. In design, the chemical quality of the water to be treated is determined experimentally, chemical addition and seed concentration are specified, a value for k_G is assumed and the time behaviour of the pH and all the species have to be determined. Time behaviour may be calculated by numerical integration of Eq. (3.36) in conjunction with the ancillary equations for species distribution. A computer programme, SOLDIV (Appendix 10), was developed to perform the integration, using values of initial reactant and seed mass concentrations and the experimentally determined rate constant (from Exp. 35H). The measured and derived values of pH and calcium species versus time are compared with predicted values in Figure 3.25. In Figure 3.26 the experimentally derived and predicted kinetics plots are compared.

It would appear that provided a reliable value of k_G is available the progress with time of the crystallization process can be closely predicted for a wide range of initial reactant concentrations and for crystal seed concentrations greater than 100 mg ℓ^{-1} in the temperature range 10 to 40°C.

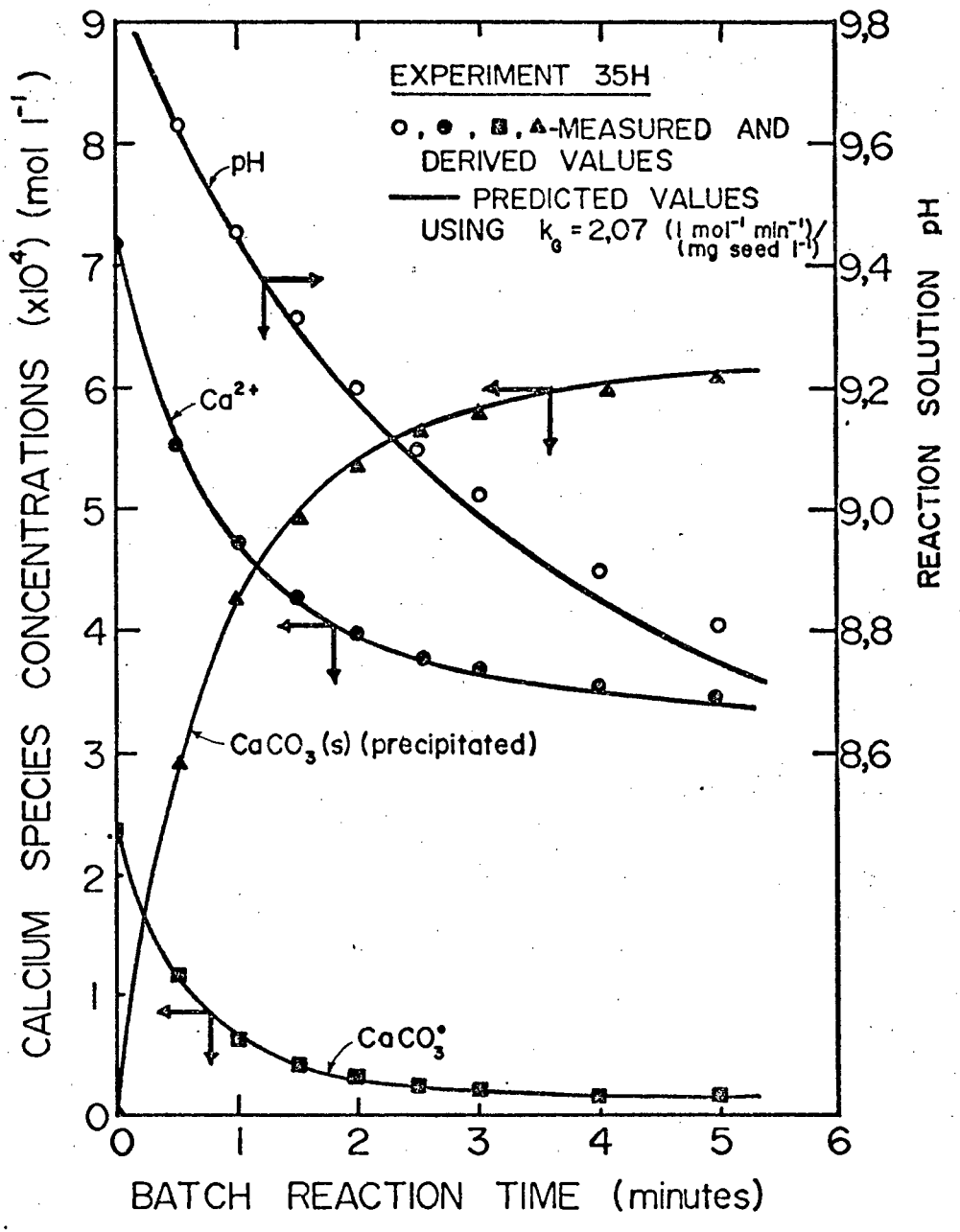

Figure 3.25. Comparison between experimental and predicted changes in pH and calcium species concentrations with time during heterogeneous $CaCO_3$ precipitation

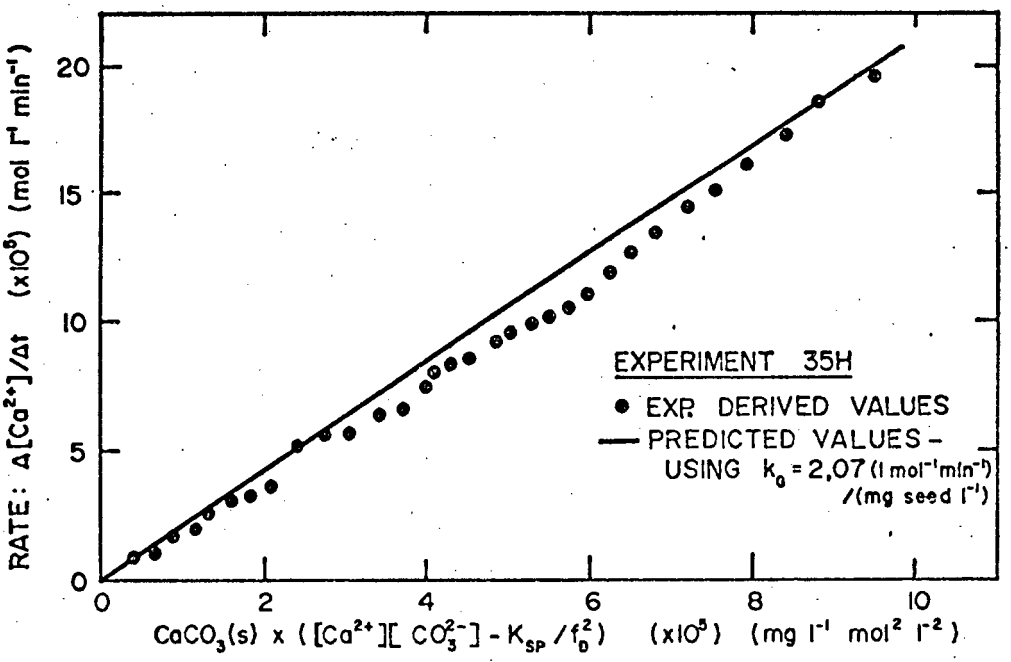

Figure 3.26 Comparison between experimentally derived and predicted kinetic plots

5.4 Conclusions

(1) The process of $CaCO_3$ batch crystallization can be monitored by measuring only pH with time. The procedure is valid provided the pH does not exceed approximately 10. At higher pH values two parameters are required, for example Ca_T^{2+} and pH.

(2) In any particular experiment, the crystallization process appears to be described adequately by the model for Ca_T^{2+} removal proposed by Reddy and Nancollas (1971), i.e.

$$\frac{d[Ca_T^{2+}]}{dt} = k_G.CaCO_3(s).\{[Ca^{2+}][CO_3^{2-}] - \frac{K_{sp}}{f_D^2}\} \quad \ldots \quad (3.42)$$

where the concentrations of Ca^{2+} and CO_3^{2-} are calculated taking ion-pairing and activity factors into consideration. Equation (3.42) satisfactorily describes individual experiments for Ca^{2+} and CO_3^{2-} concentrations ranging from $1,40 \times 10^{-4}$ to $3,29 \times 10^{-3}$ mol ℓ^{-1} and $1,83 \times 10^{-4}$ to $5,29 \times 10^{-4}$ mol ℓ^{-1}, respectively, and calcium carbonate seed crystal concentrations ranging from 100 to 1000 mg ℓ^{-1}, i.e. typical ranges for these parameters in water softening practice.

(3) There is some doubt concerning the applicability of the Reddy and Nancollas (1971) equation as a general model. The value of k_G appears to be a function of the initial pH, i.e. the pH at the start of each batch experiment. This observation leads to a contradiction in the behaviour described by Eq. (3.42), for in two experiments where the initial pH value in one experiment occurs at some point during precipitation in the other, the rates of precipitation, $(d[Ca^{2+}]/dt)$, are not identical. Modification of the rate Equation (3.42) as proposed by Sturrock, Benjamin, Loewenthal and Marais (1976), to

$$\frac{\delta[CaCO_3]}{\delta t} = k_G.M.f_D^2 \{[Ca^{2+}]^{\frac{1}{2}}[CO_3^{2-}]^{\frac{1}{2}} - (\frac{K_{sp}}{f_D^2})^{\frac{1}{2}}\}^2 \quad .... \quad (3.43)$$

appears to resolve these inconsistancies.

(4) The crystallization rate constant, k_G, is temperature dependent according to the Arrhenius relationship, i.e.

$$k_G = A.e^{-E/RT} \quad .... \quad (3.44)$$

where E = activation energy
= $10,3 \pm 0,9$ kcal mol^{-1}

(5) The rate constant, k_G, is independent of the stirring speed and the crystal seed concentration.

(6) The high activation energy, the independence of k_G on stirring speed and the second order dependence of the rate of $CaCO_3$ precipitation on the supersaturation term, all support a surface controlled mechanism for $CaCO_3$ crystal growth. Although the rate of precipitation is dependent on the total surface area and the available crystallization sites, this investigation showed that the mass of crystals can substitute for the surface area. As the surface to mass ratio will differ between crystals of different origin, the k_G value cannot yet be determined *ab initio*, but must be determined by experiment.

(7) Knowing only the initial reactant inputs and the seed mass, together with a reliable estimate of k_G, it is possible to predict batch system $CaCO_3$ crystallization time behaviour.

6. HETEROGENEOUS $CaCO_3$ PRECIPITATION IN CSTR SYSTEMS

In practice batch precipitation processes are usually limited to small-scale applications. The more commonly used processes are the continuous precipitation processes. In such systems the chemicals are added to a raw water stream, are thoroughly mixed and reacted with the water, usually in a back mix reactor, and the resultant suspension is flocculated and clarified in a sedimentation unit. To simulate these practical processes in the laboratory using pure synthetic systems requires the study of $CaCO_3$ precipitation in completely stirred tank reactor systems in the presence of seed crystals, i.e. heterogeneous $CaCO_3$ precipitation.

The work reported in this section was not performed by the author, but by another student working in the same research team at the University of Cape Town. Sturrock (1975) reported his findings in his M.Sc.(Eng.) thesis entitled "Calcium carbonate precipitation kinetics".

6.1 Materials and Methods

The materials and methods used by Sturrock (1975) were similar to those reported in the previous section, the only difference being that the tests were conducted in CSTR systems rather than in batch reactors.

Two feed tanks were connected to the batch reactor. One tank contained a carbonate solution ($NaOH + NaHCO_3$) and the other a calcium solution ($CaCl_2$) together with $CaCO_3$ seed crystals (HOPKIN AND WILLIAMS, Analar brand) at a concentration of 1800 mg ℓ^{-1} (see Figure 3.27). The seed crystals were kept in suspension in the feed tank by means of a magnetic stirrer. Solutions from each tank were pumped at equal ratios into the reactor and the pH of the reactor contents was monitored.

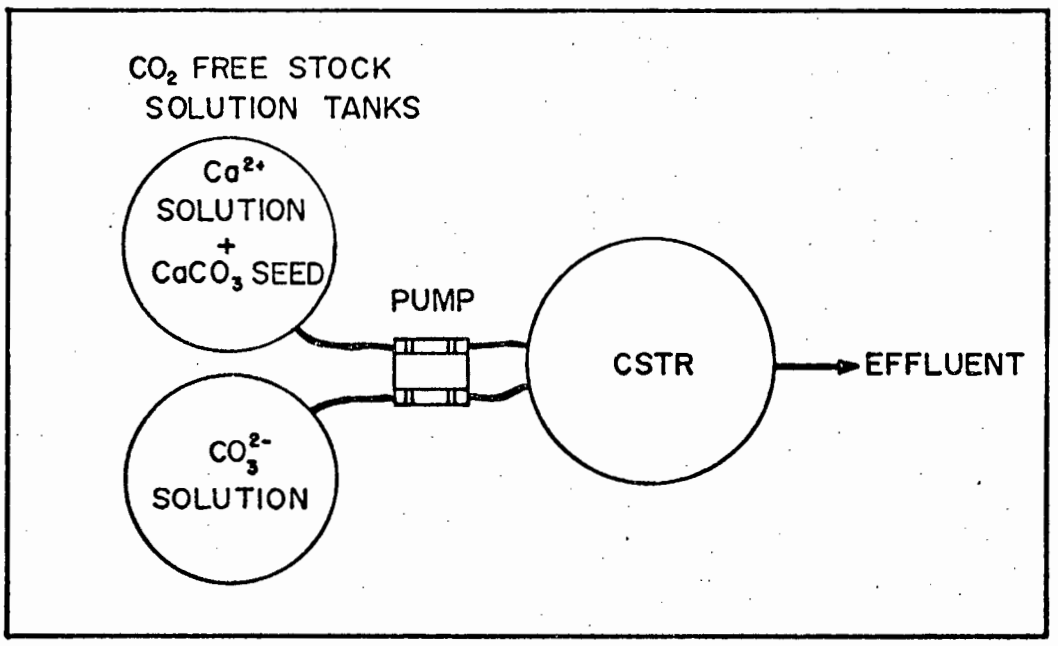

Figure 3.27 Schematic diagram of apparatus used in steady state tests

For any given hydraulic retention time the flow was maintained until the pH attained a steady reading and remained steady for a period of two retention times. The influent feeds were then stopped and the decrease in pH with time was recorded for a period until the pH showed no significant change. The feed flows were then restarted to give a different hydraulic retention time in the reactor.

At any particular steady state, knowing only the pH, temperature, alkalinity and concentration of Ca_T^{2+} of the influent feeds, it is possible to determine each of the parameters in the following equation,

$$\frac{\delta[CaCO_3]}{\delta t} = k_G.M.f_D^2\{[Ca^{2+}][CO_3^{2-}] - \frac{K_{sp}}{f_D^2}\} \quad \ldots. \quad (3.45)$$

which is a slightly modified form of Eq. (3.42) (to incorporate activity factors more precisely). Consequently, the $CaCO_3$ supersaturation at steady state can be calculated. Also when the feed flow was stopped, the rate of precipitation could be calculated, the initial rate giving an estimate of the rate at that particular steady state. By this means a value for reaction constant, k_G, was determined for each steady state.

6.2 Results and Discussion

Typical results for the rate constant, k_G, for heterogeneous $CaCO_3$ precipitation in CSTR systems are listed in Table 3.10. These results are very similar to those found for heterogeneous $CaCO_3$ precipitation in batch systems, as listed in Table 3.11. It can thus be concluded that batch systems form a reasonable basis for the study of various effects on heterogeneous $CaCO_3$ precipitation, such as pH, temperature and supersaturation.

As reported in the previous section, the absolute value of k_G may be different for $CaCO_3$ crystals from different chemical suppliers. Similarly, $CaCO_3$ particles precipitated in different lime treatment plants may also have different k_G values. Therefore, before applying Eq. (3.45) for design purposes, k_G values specific to the process

Table 3.10

Experimental and derived data for heterogeneous $CaCO_3$ precipitation in CSTR systems

Exp. No.	Steady State Supersaturation (mg ℓ^{-1} as $CaCO_3$)	Seed Mass (mg ℓ^{-1})	Reaction Constant, k_G $(min)^{-1}$. (mg ℓ^{-1} as $CaCO_3)^{-1}$
1	1220	900	2,58
	533	915	2,30
	434	919	2,30
	353	923	2,00
	242	927	1,70
	199	929	1,15
2	542	914	2,30
	224	927	1,70
	175	930	1,15
3*	829	900	1,05
	639	912	0,96
	450	918	0,84
	316	922	1,00
	247	925	0,90

*Batch B of seed crystals

under consideration should be established by continuous laboratory pilot-scale tests.

Sturrock (1975) reported no scale formation problems for seeded $CaCO_3$ precipitation in CSTR systems. This observation is of importance, since scale formation takes place at an unacceptably high rate in experiments where no seed crystals were added (see Section 4.2).

Table 3.11

Experimental and derived data for heterogeneous $CaCO_3$ precipitation in batch systems

Exp. No.	Initial pH	Initial $CaCO_3$ Supersaturation (mg ℓ^{-1} as $CaCO_3$)	Seed Mass (mg ℓ^{-1})	Reaction Order, n	Reaction Constant $(min)^{-1}$ (mg $^{-1}$ as $CaCO_3)^{-1}$
1	8,60	135	900	0,89	1,16
2	8,72	166	900	0,72	1,09
3	9,34	241	900	0,72	1,41
4	8,90	245	900	0,79	1,36
5	9,20	279	900	0,97	1,43
6	9,61	287	900	1,06	1,71
7	8,88	301	900	1,00	1,85
8	9,55	308	900	0,89	1,75
9	9,00	320	900	0,90	1,65
10	9,95	463	900	0,98	2,16
11	9,20	482	900	0,93	2,20
12	9,18	529	900	0,96	2,10
13	9,56	616	900	1,01	2,30
14	8,83	630	900	0,90	2,10
15	9,37	656	900	0,98	2,40
16	9,50	740	900	0,95	2,40
17	9,48	754	900	1,06	2,60
18	9,05	786	900	0,94	2,26
19	9,62	952	900	1,04	2,63
20	9,60	995	900	1,02	2,65
21	9,61	1000	900	1,02	2,80
22	9,73	1200	900	1,02	2,91
23	9,83	1210	900	0,99	3,00
24	9,77	1304	900	1,04	2,85
25	9,59	1623	900	1,00	3,00
26	10,00	2061	900	1,06	3,07
27	10,13	2190	900	1,18	2,90
28	9,68	2443	900	0,97	2,75
29	10,30	2500	900	1,12	2,75
30	10,28	2227	1500	1,08	2,72
31	10,00	1290	1500	1,05	2,75
32	9,80	1250	1500	1,06	2,90
33	9,77	905	1500	1,01	2,56
34	9,64	888	1500	0,97	2,65
35	9,35	627	1500	0,99	2,10
36	9,65	954	300	1,06	2,75
37	9,36	697	300	1,00	2,57
38 *	9,78	840	900	0,95	1,02

*Batch B of seed crystals

6.3 Conclusions

(1) The Reddy and Nancollas (1971) model for $CaCO_3$ precipitation kinetics (Eq. 3.36) holds for both batch and CSTR reactor systems.

(2) Using HOPKIN and WILLIAMS Analar grade $CaCO_3$ seed crystals, the value for the rate constant obtained for CSTR systems is in good agreement with that for batch systems. However, due care must be observed in applying laboratory determined k_G values to systems producing self-seeding mass, in say full-scale plants where precipitated sludge is recirculated.

(3) Crystal seeding in CSTR systems greatly reduces the problem of scale formation on the reactor walls.

7. GENERAL CONCLUSIONS ON THE PURE SYSTEM $CaCO_3$ PRECIPITATION INVESTIGATION

The major findings of the investigation into pure system $CaCO_3$ precipitation may be summarized as follows :

(1) By monitoring only pH with time it is possible to obtain a complete description of the progress of the $CaCO_3$ precipitation reaction with time. This procedure requires that the dissociation constants for the various ionic equilibria be known and that ionic equilibrium is established very rapidly relative to precipitation. Values for all the relevant constants are available in the literature and it was experimentally demonstrated that the ionic reactions are extremely rapid.

(2) Precipitation behaviour of the pure system indicates that in two-stage recarbonation processes without crystal seeding (sludge recirculation), severe scale formation in static mixers and on reactor walls and impellers may be expected. In addition, difficulties may be encountered with the separation of the precipitant from the reactor effluent suspension. Both scaling intensity and efficiency of precipitant - effluent separation may be improved by the addition of seed crystals to the reaction phase.

(3) The crystallization model of Reddy and Nancollas (1971) although explaining certain features of $CaCO_3$ precipitation in individual tests, does not appear to be generally applicable and leads to apparently contradictory precipitation behaviour. A rate equation proposed by Sturrock, Benjamin, Loewenthal and Marais (1976) overcomes this problem and hence gives a generalized description of $CaCO_3$ precipitation kinetics.

At this stage of the investigation a decision had to be taken on the research avenue which could most fruitfully be pursued following on from the pure system calcium carbonate precipitation studies. A logical progression from the work reported in this chapter would have been a systematic study of magnesium hydroxide and tricalcium phosphate precipitation from pure synthetic solutions. This could have been followed by a study of the co-precipitation of $CaCO_3$, $Mg(OH)_2$ and $Ca_3(PO_4)_2$ from synthetic solutions and their mutual interaction.

However, the main impetus and stimulus for this project was derived from the urgent need for design criteria for lime treatment of sewage effluents. For this reason it was decided to redirect the investigation from a fundamental to a more practical approach, i.e. an investigation into the precipitation reactions which take place in the lime treatment of sewage effluents.

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CHAPTER 4

LIME TREATMENT OF WASTE WATER - LABORATORY STUDIES

1. GENERAL INTRODUCTION

Following on the work on pure systems, laboratory studies were inaugurated to obtain information on precipitation in effluents from sewage works. The most widely used chemical additive for obtaining both inorganic and organic material precipitation is lime. This chapter deals primarily with laboratory studies designed to determine the response of secondary effluent to lime treatment.

Any study of the lime treatment of waste water must take into consideration the chemical and physical-chemical reactions which take place subsequent to the addition of lime to the waste water. The major chemical reactions are likely to be (Bernhoff, 1974; Merrill, 1974),

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^- \quad .... \quad (4.1)$$

$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O \quad .... \quad (4.2)$$

$$OH^- + H_2PO_4^- \longrightarrow HPO_4^{2-} + H_2O \quad .... \quad (4.3)$$

$$OH^- + NH_4^+ \longrightarrow NH_4OH \quad .... \quad (4.4)$$

$$3\,Ca^{2+} + 2H_2PO_4^- + 4OH^- \longrightarrow Ca_3(PO_4)_2(s)^* + 4H_2O \quad .... \quad (4.5)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3(s) \quad .... \quad (4.6)$$

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2(s) \quad .... \quad (4.7)$$

$$NH_4OH \longrightarrow NH_3(g) + H_2O \quad .... \quad (4.8)$$

$$CO_2(g) + 2OH^- \longrightarrow CO_3^{2-} + H_2O \quad .... \quad (4.9)$$

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* There is no clarity in the literature as to the actual form in which phosphate is precipitated. In the recent literature (Merrill, 1974; Ferguson, Jenkins and Stumm, 1970) tricalcium phosphate appears to be the most favoured form.

In addition to these chemical reactions, it is known that a number of adsorption reactions may take place once the solid precipitates have formed (Griffin and Jurinak, 1973; Black and Christman, 1961). The following are some possible hypothetical adsorption equations,

$$n_1 HPO_4^{2-} + m_1 CaCO_3(s) \longrightarrow \langle n_1 HPO_4^{2-} \rangle --- \langle m_1 CaCO_3(s) \rangle \quad .... \quad (4.10)$$

$$n_2 Mg^{2+} + m_2 CaCO_3(s) \longrightarrow \langle n_2 Mg^{2+} \rangle --- \langle m_2 CaCO_3(s) \rangle \quad .... \quad (4.11)$$

where n_1, n_2, m_1, m_2 are intergers.

Other reactions which may take place are sequestration of the Ca^{2+} and Mg^{2+} and disinfection reactions. All these reactions take place simultaneously, albeit at different rates and often in competition for the same reaction species. It is therefore clear that a comprehensive study of lime-waste water systems is a formidable undertaking.

A review of the pertinent literature on lime precipitation reactions in waste waters is reported in Chapter 2. From this review and from practical problems experienced with lime treatment as applied in the water reclamation process at the Stander Water Reclamation Plant (Pretoria, South Africa), four specific aspects related to lime reactions were identified as critical problem areas requiring urgent investigation. These were,

(1) lime dissolution kinetics,
(2) batch lime treatment of secondary effluent,
(3) continuous lime treatment of secondary effluent, and
(4) characterization of lime-treated effluents.

Each of these specific topics is dealt with separately in the following four sections.

2. LIME DISSOLUTION KINETICS

In the lime treatment of waste water the lime is commonly dosed to the water in the form of a slurry. The calcium and hydroxide components in the $Ca(OH)_2$ slurry cannot react until these are in the dissolved form, i.e. until $Ca(OH)_2$ is dissolved. Dissolution kinetics of the solid lime is therefore of importance to the process. This aspect is seldom considered in the many papers reported in the literature on lime treatment.

Mennell, Merrill and Jorden (1974) and Merrill (1974) have considered the effect of incomplete lime dissolution on treated effluent turbidity and residual phosphate (see Chapter 2, Section 5.2). They presented a practical solution to the problem by applying "split"-stream lime treatment and high intensity mixing in the "split" chamber. However, no quantitative data was presented relating the degree (or percentage) lime dissolution to dissolution time.

Jenkins and Lee (1976) proposed and tested a model for lime dissolution kinetics (see Chapter 2, Eq. (2.61)),

$$\log (1 - [OH^-] / [OH^-]_\infty) = k.t \qquad \ldots\ldots \quad (4.12)$$

As pointed out in the literature survey this equation does not model lime dissolution *per se*, but rather the kinetics of the net increase in hydroxide ion concentration with time. Nevertheless, this equation provides a practical solution for predictive purposes in the design of lime reaction systems.

In this investigation the applicability of the Jenkins and Lee model was investigated for the range of lime concentrations usually associated with full stream waste water lime-treatment, i.e. 0-500 mg ℓ^{-1} (as $Ca(OH)_2$).

2.1 Methods

Lime dissolution kinetics was studied for de-ionized water and secondary effluent at 20°C. The solution being studied was syphoned into a perspex reaction vessel (Reactor R2, see Appendix 5). A perspex stirring rod with four blades was used for mixing the solution at 60 rpm. Two pH electrodes (glass and calomel) were calibrated using NBS standard buffers and were suspended in the solution from the reactor cover. A lime slurry (± 5 percent) was rapidly injected into the stirred solution (±1 sec) by means of a hypodermic syringe. The change in pH accompanying the dissolution of the lime was measured continuously and monitored on a stripchart recorder (Hewlett Packard 7100 BM). The net rate of increase of the hydroxide ion concentration with time was determined for lime dosages ranging from 50 to 450 mg ℓ^{-1}.

In all these studies the lime used was a commercial grade air-separated hydrated lime. Typical analyses supplied by the lime manufacturer and determined in our laboratories are listed in Table 4.1. The discrepancies between these analyses illustrate the importance of regular analysis of new batches of lime in order to assess if the lime conforms to the specifications agreed to by the supplier. Also, regular checking of the active content of existing stocks of lime will indicate the rate of deterioration of lime (loss of active lime) with time.

Table 4.1

Typical analyses for commercial grade air-separated lime

Parameter	Expressed as	Percentage by Weight	
		Lime Producer	Our Laboratory
Available $Ca(OH)_2$	CaO	67,7	61,5
Total $Ca(OH)_2$	CaO	73,9	63,2
Magnesium	MgO	0,9	0,5
Silica	SiO_2	1,4	0,5
Mn, Al, Fe	R_2O_3	0,9	-
Loss on ignition	-	22,9	-

Secondary sewage effluent used in this investigation was obtained from the Humus Tank effluent stream of the Daspoort Sewage Works (Pretoria, South Africa). This effluent may be classified as a biologically stable biofilter effluent. The same effluent source was used as the raw water source for the Stander Water Reclamation Plant. Typical analyses showing effluent quality variations over a period of a year are listed in Table 4.2.

2.2 Results and Discussion

Lime dissolution studies were preceded by tests for establishing the pH measuring system's response to changes in pH. The rate of response of the system to rapid changes in pH was determined by measuring pH changes with time on the addition of an aliquot of a strongly alkaline solution (1,0 N NaOH) to deionized water. Since sodium hydroxide is completely dissolved in water, no time is required for dissolution and the measured changes in pH with time are only a function of the mixing intensity in the batch reactor and the response characteristics of the pH electrodes and the rest of the pH measurement equipment.

A typical recorder trace (trace H20, Figure 4.1) illustrates the measuring system's response for 20 seconds after the sodium hydroxide solution addition to the deionized water. The first measurable pH change was observed after one second. This period corresponds to the time required for alkali injection and for the reactor mixer to disperse the alkali throughout the de-ionized water in the reactor. Another second was required for the pH to stabilize. This period corresponds to the time required for the pH electrodes to respond to the pH change and to stabilize. Recorder traces for the addition of lime slurry to deionized water (trace H12, Figure 4.1) and secondary effluent (trace H23, Figure 4.1) display similar characteristics for the first second response. However, the pH does not stabilize after two seconds, but steadily increases with time due to the lime dissolution.

Table 4.2

Typical average weekly analyses for Pretoria Municipal Sewage Works humus tank effluent

Analysis/Date	26-30/3/75	5-11/5/75	7-13/7/75	8-14/9/77*
Temperature (^{o}C)	21,9	19,5	16,2	20,4
pH	7,68	7,89	7,58	7,62
Total Alkalinity (as $CaCO_3$)	158	172	158	213
Total Hardness (as $CaCO_3$)	163	184	200	177
Ortho-Phosphate (as PO_4-P)	6,3	6,5	6,1	7,4
COD (as O)	14	23	37	40
Ammonia (as NH_3-N)	7,7	6,8	9.1	15,1
Nitrate as (NO_3-N)	11,8	13,0	12,9	5,8

*Biofilters in poor condition due to poisoning of microbio-mass on filters

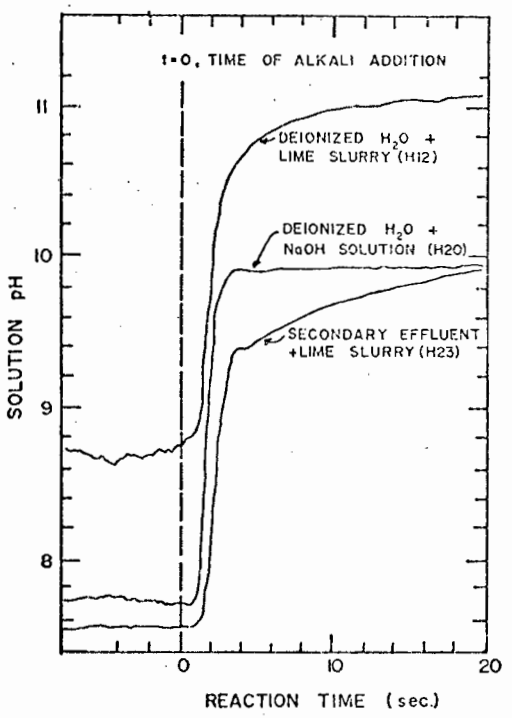

Figure 4.1. Reponse of pH electrodes and measuring system to alkali addition

pH-time curves for the dissolution of various concentrations of lime (56-333 mg ℓ^{-1}) in deionized water are shown in Figure 4.2. It is clear from these plots that lime does not dissolve instantaneously in deionized water.

pH-time curves for lime dissolution (56-417 mg ℓ^{-1}) in secondary effluent are shown in Figure 4.3. The changes in pH with time, for equivalent quantities of lime, required four to six minutes to stabilize in secondary effluent as compared to the two to three minutes required for lime dissolution in deionized water. This difference can be explained as follows : Lime dissolves in deionized water to form only calcium and hydroxide ions (neglecting ion pairing),

$$Ca(OH)_2(s) \longrightarrow Ca^{2+} + 2OH^- \quad \ldots\ (4.13)$$

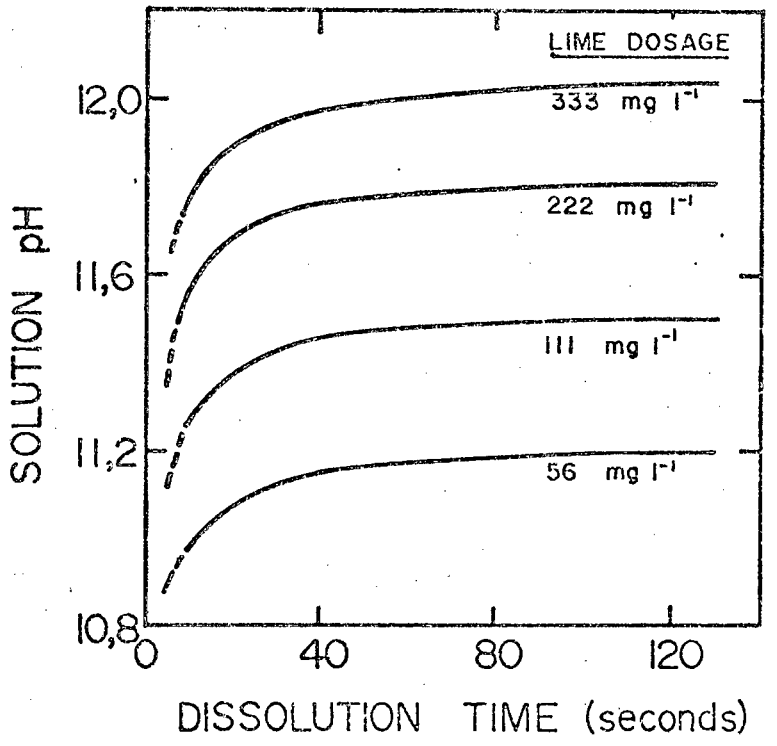

Figure 4.2. pH changes with time for $Ca(OH)_2$ dissolution in deionized water.

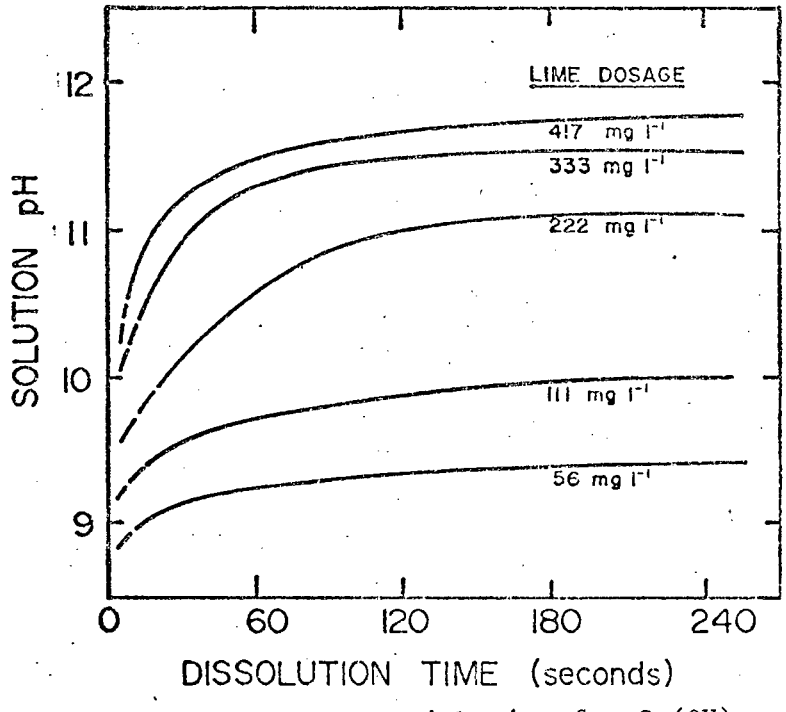

Figure 4.3. pH changes with time for $Ca(OH)_2$ dissolution in secondary effluent.

Therefore, the solution pH is controlled only by the OH^- ions released by the dissolving lime. However, in the case of secondary effluent the hydroxide ions react with other ions present in the effluent, i.e.

$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O \quad .... \quad (4.14)$$

$$OH^- + H_2PO_4^- \longrightarrow HPO_4^{2-} + H_2O \quad .... \quad (4.15)$$

$$OH^- + NH_4^+ \longrightarrow NH_4OH \quad .... \quad (4.16)$$

$$4OH^- + 2H_2PO_4^- + 3Ca^{2+} \longrightarrow Ca_3(PO_4)_2(s) + 4H_2O \quad .... \quad (4.17)$$

$$2OH^- + Mg^{2+} \longrightarrow Mg(OH)_2(s) \quad .... \quad (4.18)$$

The pH-time curves therefore represent the net increase of hydroxide ions with time rather than the rate of lime dissolution. It is also possible that precipitation and adsorption of substances from the secondary effluent may take place on the dissolving lime particles, thereby hindering lime dissolution. Comparing Figures 4.2 and 4.3 it appears that the net effect of the heterogeneous components of secondary effluent is a reduction in the rate of lime dissolution.

The model for lime dissolution kinetics proposed by Jenkins and Lee (1976), Eq. (4.12), was applied to the experimental data. Plots of $\log (1-[OH]/[OH^-]_\infty)$ versus time for lime dissolution in deionized water and secondary effluent are shown in Figures 4.4 and 4.5, respectively.

The model fits poorly the experimental data for lime dissolution in deionized water. The kinetic plots are curved lines (see Figure 4.4) rather than straight line plots as predicted by the model. However, the model does fit the experimental data for lime dissolution in secondary effluent (Figure 4.5), i.e. the kinetic plots are linear and pass through the origin. Rate constants determined from the

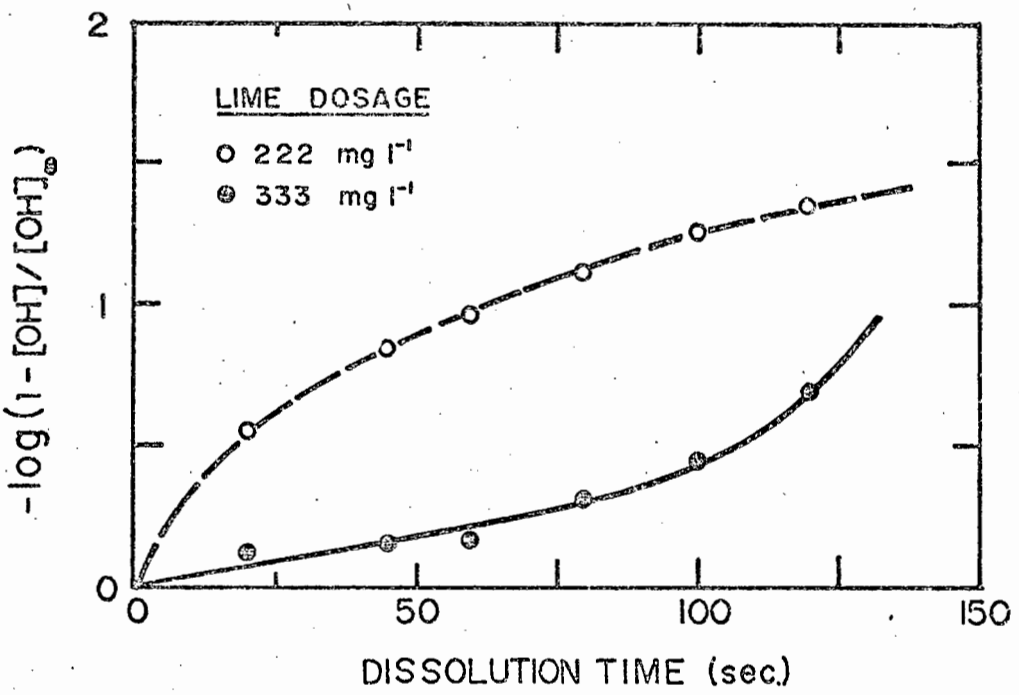

Figure 4.4. Kinetic plot for lime dissolution in deionized water.

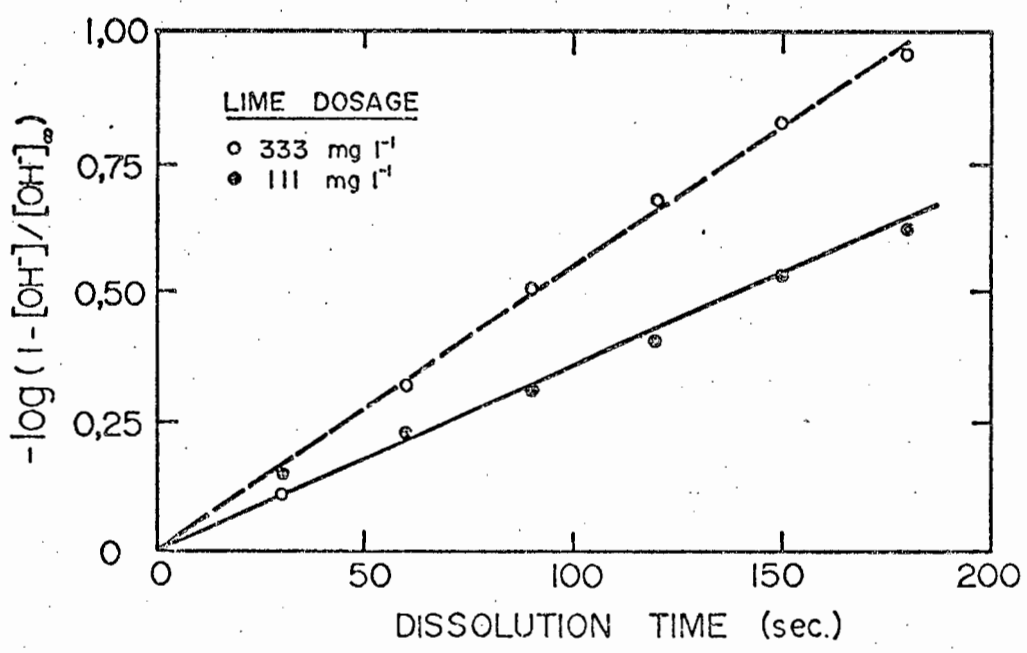

Figure 4.5. Kinetic plot for lime dissolution in secondary effluent.

Table 4.3

Rate constants for lime dissolution

Lime Concentration (mg ℓ^{-1})	Final pH	Rate Constant (min^{-1})
	DEIONIZED WATER	
56	11,22	1,00
111	11,55	0,83
222	11,83	0,96
333	12,50	0,28
	SECONDARY EFFLUENT	
56	9,50	0,28
111	10,10	0,21
222	11,20	0,21
333	11,60	0,28
417	11,85	0,94

slopes of these plots are listed in Table 4.3 (For the purpose of comparison estimates of rate constants for lime dissolution in deionized water are also listed). Experimentally determined rate constants for lime dissolution in secondary effluent, with the exception of the experiment in which a very high lime dosage was used (417 mg ℓ^{-1}), were relatively constant ranging from 0,21 to 0,28 (min^{-1}). For predictive purposes average k values of 0,77 and 0,21 (min^{-1}) were accepted for de-ionized water and secondary effluent, respectively. Figure 4.6 illustrates the relationships between fraction of lime dissolved (or more correctly, fraction of total hydroxide ions dissolved) as a function of time. As a typical example, for 80 percent lime dissolution it is predicted that 1,6 minutes are required in de-ionized water and 4,6 minutes in secondary effluent.

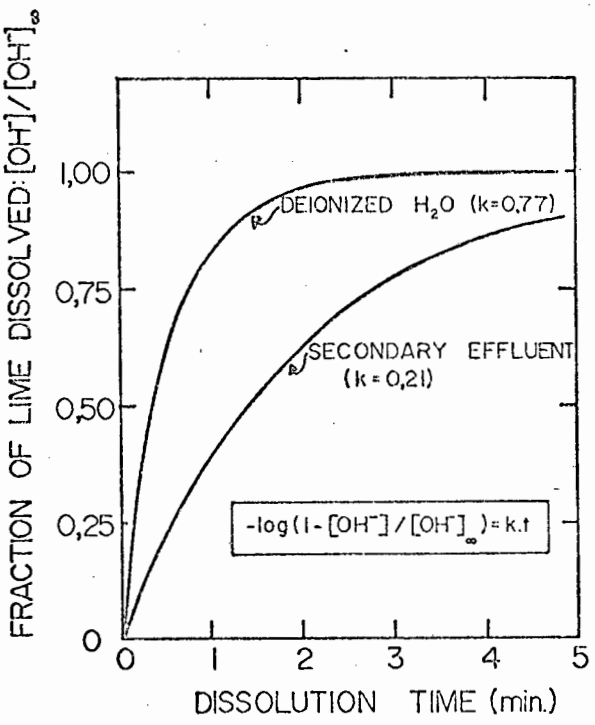

Figure 4.6. Predicted lime dissolution rates

The k values determined in this study for de-ionized water and secondary effluent, 0,77 and 0,21 min^{-1}, respectively, are considerably lower than the values of 1,0 and 0,42 min^{-1} found by Jenkins and Lee (1976) for de-ionized water and raw waste water. The differences may be explained in terms of the higher lime concentrations used by these authors, i.e. 2000 mg ℓ^{-1} as against 56-417 mg ℓ^{-1} used in this study, resulting in a greater driving force and hence more rapid dissolution. Due to inherent simplifications in Eq. (4.12) this model cannot be generalized for different effluents nor applied to data obtained under different experimental conditions. The model is essentially empirical and the constants in the relationship should be determined for each effluent under conditions as close as possible to those actually expected. Notwithstanding these limitations the model serves a useful purpose for qualitative predictions relating to lime dissolution kinetics.

It is clear from the qualitative predictions made using Eq. (4.12) that lime dissolution in secondary effluent is time dependent and requires 5 or more minutes to attain an essentially stable dissolution state in batch reactors. Practical solutions to overcome this problem have been proposed by Mennell, Merrill and Jorden (1974) and Jenkins and Lee (1976). Mennell *et al* suggested the use of "split" lime treatment, i.e. essentially completely dissolving the lime in a split stream (± 15 percent) of the main stream, before adding it to the main stream. Jenkins and Lee suggested essentially complete lime dissolution in a small recycled stream (± 15 percent of baseflow) from the clarifier overflow, the advantage being that lime dissolution is less inhibited in treated effluent than in raw effluent.

Although both these methods lead to improved efficiency, there may be other procedures of equivalent efficiency. In this investigation (see Section 4.4) the use of static mixers in conjunction with sludge recirculation was tested.

2.3 Conclusions

(1) The Jenkins and Lee (1976) model for batch lime dissolution,

$$- \log (1 - [OH]/[OH]_{\infty}) = k.t \quad \ldots\ldots (4.19)$$

failed in predicting lime dissolution in deionized water for lime concentrations associated with full-scale lime treatment, but gave acceptable results for lime dissolution in secondary effluent.

(2) The model represented by Eq. (4.19) may be used for estimating minimum batch reaction times required for dissolving a pre-selected percentage of lime. Reaction times required for CSTR systems are dealt with later in Section 4.

3. BATCH LIME TREATMENT - TIME BEHAVIOUR STUDIES

Reviewing the literature on the lime treatment of sewage effluent, very few references were found on batch reactor time-behaviour studies. This is perhaps not surprising since batch lime treatment is seldom used in practice. However, the importance of batch reactor time behaviour studies lies in the information they provide as to the minimum time required to achieve a stable effluent.

Merrill and Jorden (1974) reported on the batch reaction of raw sewage with lime dosages of 150 to 350 mg ℓ^{-1} (as $Ca(OH)_2$). They found the soluble concentrations of PO_{4T}^{3-}, Ca_T^{2+}, $CO_{3.T}^{2-}$ and Mg_T^{2+} to be essentially stabilized within $2\frac{1}{2}$ minutes following lime addition. However, for complete reaction up to 24 minutes or longer were required (see Chapter 2, Section 5.2).

In this section the time behaviour of lime-treated effluent in the absence of any added sludge or seed crystals is considered. The study attempts to determine minimum periods required for effluent stabilization. Unseeded experiments have the advantage that the $CaCO_3$ and $Mg(OH)_2$ precipitation reactions are slow enough to be followed by the simple experimental technique of precipitation reaction quenching by filtration. In the presence of sludge, as will be shown in Section 4, the precipitation reactions are so rapid that they cannot be followed by this technique.

3.1 Methods

A batch lime treatment experiment was conducted as follows : Secondary effluent was poured into a batch reactor, a 1,0 ℓ glass beaker. A predetermined volume of lime slurry was added to the effluent. The mixture was vigorously agitated by means of a magnetic stirrer to disperse and dissolve the lime in the secondary effluent. This was followed after approximately 5 minutes by gentle stirring, sufficient to keep the suspended matter dispersed throughout the solution, but not vigorous enough to cause air entrapment with accompanying

reaction with CO_2 from the air. Samples (10 mℓ) were withdrawn from the reaction solution at regular intervals, at 1; 2; 3; 4; 5; 7; 10; 15; 30; 60 and 90 minutes and immediately (<5 sec) vacuum filtered (Whatman No 42 filter paper). The receiving vacuum flask contained two drops of concentrated hydrochloric acid to quench any further precipitation from the filtrate. The acidified samples were analysed for calcium and magnesium (by an atomic absorption analytical technique). These values corresponded to residual dissolved calcium and magnesium in the reaction mixture at the time of filtration. Where time allowed, i.e. when sampling at 30, 60 and 90 minutes, larger samples were taken and analysed more extensively, i.e. for temperature, pH, total alkalinity, total and residual calcium and magnesium.

Batch precipitation of both $CaCO_3$ and $Mg(OH)_2$ from secondary effluent was studied for a range of lime dosages, corresponding to initial pH values ranging from 10,0 to 11,8. The experiments were conducted at ambient temperatures ranging from 20 to 25°C. Raw data collected during this study are listed in Appendix 8.

3.2 Results and Discussion

Typical results for batch lime-treated secondary effluent are shown in Figure 4.7, i.e. plots of pH and residual total dissolved calcium and magnesium versus time.

pH-reaction time relationship

Changes in the pH with time for batch-treated effluent have been discussed in detail in the previous section. These relate mainly to lime dissolution (increases in pH) and to a lesser extent to the precipitation reactions (decreases in pH). Effluent pH values stabilized between two to five minutes after lime addition. The effluents displayed slowly decreasing pH values for long reaction times, possibly due to reaction with CO_2 from the air.

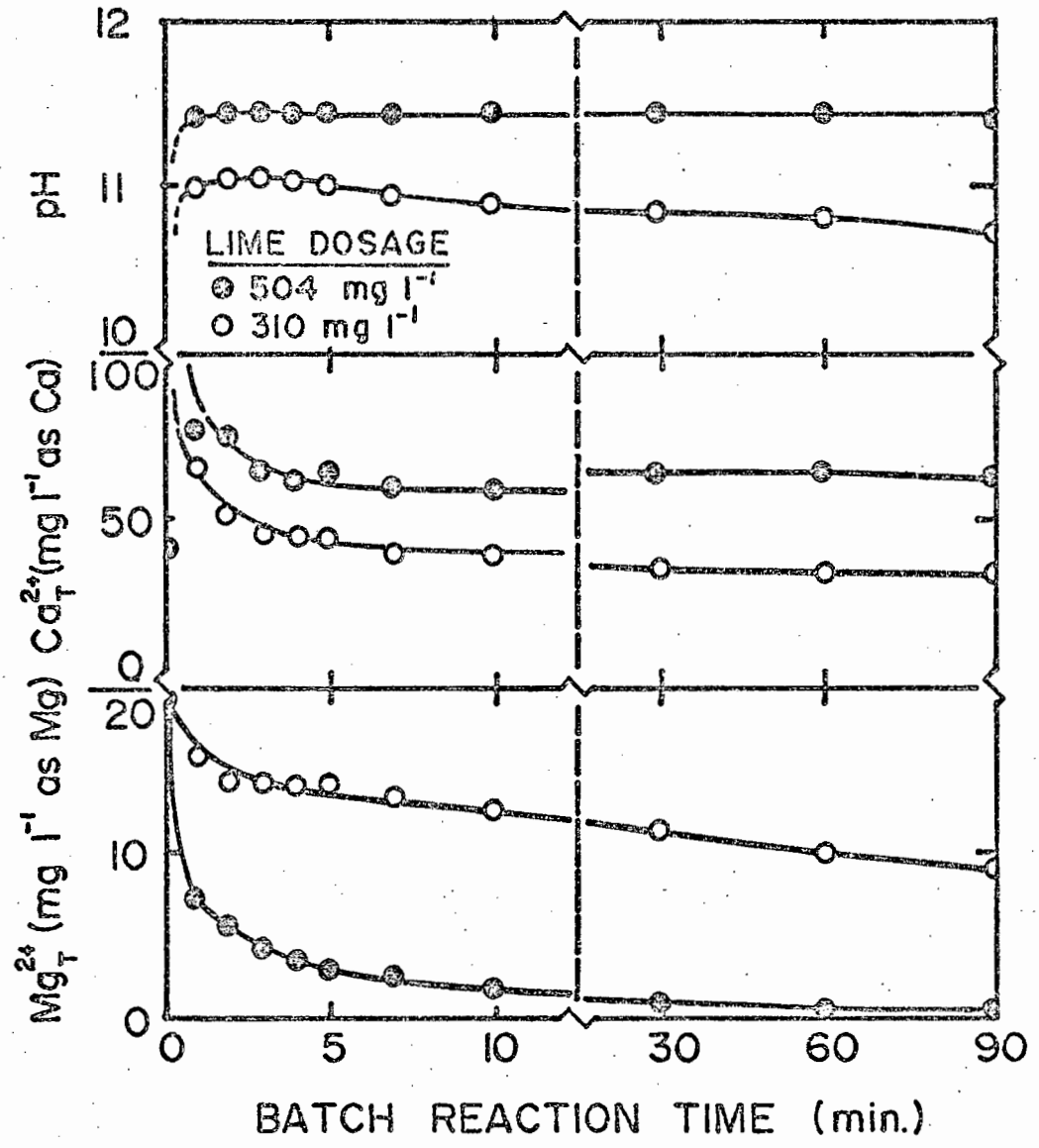

Figure 4.7. Lime-treated secondary effluent batch precipitation

Residual calcium - reaction time relationship

Typical changes in residual total dissolved calcium with time for batch lime-treated secondary effluent are illustrated in Figure 4.7. It is evident from this diagram that the calcium reactions, both dissolution and precipitation are essentially complete* within three to five minutes batch reaction time. However, small but significant (10 to 30 mg ℓ^{-1} as $CaCO_3$) changes still take place up to 30 minutes and even 90 minutes batch reaction time. These results are similar to those reported by Merrill (1974) for lime-treated raw sewage.

Residual magnesium - reaction time relationship

Typical changes in residual dissolved magnesium with time are illustrated in Figure 4.7. For the whole pH range studied (10,0 - 11,8) there was rapid initial magnesium removal within the first minute after lime addition. This was followed by slower magnesium removal upto reaction times of one hour or longer.

Liu and Nancollas (1973) concluded that initial rapid removal of magnesium in pure synthetic systems is due to bulk nucleation (even in the presence of seed crystals) with a subsequent surge in the magnesium removal due to the rapid growth of these new nuclei. Slow magnesium removal is attributed to diffusion controlled crystal growth and recrystallization of the $Mg(OH)_2$. It was also noted that Merrill (1974) reported a 4-10 minutes batch retention period as essential for complete $Mg(OH)_2$ precipitation, i.e. somewhat shorter reaction times than determined in this investigation.

3.3 Conclusions

(1) Calcium reactions in unseeded batch lime-treated secondary effluent are rapid and essentially complete (>90 percent) within 3 to 5 minutes. However, small but significant quantities (10 to 30 mg ℓ^{-1} as $CaCO_3$) of calcium carbonate still precipitate

*"Essentially complete" refers to 90 percent reaction completion, with 90 minutes taken as the time required for 100 percent reaction completion.

from solutions even at reaction times of 30 minutes.

(2) Rapid magnesium removal takes place during the first minute of batch lime treatment. This is followed by slow removal over a period of an hour or longer.

(3) Conclusions (1) and (2) indicate that sludge recirculation could be usefully applied to reduce the reaction time required for producing stable effluents.

These studies were not pursued to any depth due to the limited practical value of batch lime treatment. The next section deals more comprehensively with lime treatment as applied in CSTR systems using sludge recirculation, i.e. the system more generally applied in practice.

4. CONTINUOUS LIME TREATMENT - CSTR STUDIES

Many laboratory and pilot plant studies of continuous lime treatment of waste waters have been reported in the literature. However, in most cases the emphasis has been on effluent clarification, phosphate and organic material removal. In some instances, for example the study reported by Berg, Brunner and Williams (1970) (see Chapter 2, Section 5.2), residual calcium and magnesium values as a function of pH have been reported for lime-treated waste waters. However, few detailed studies have been reported on $CaCO_3$ and $Mg(OH)_2$ precipitation *per se* in continuously stirred tank reactor (CSTR) systems for lime treatment processes.

The three major process variables which influence precipitation and effluent quality in continuous lime treatment are,

(1) CSTR residence time,

(2) lime dosage (pH), and

(3) sludge concentration.

On full-scale plants there are usually some physical limitations to making extensive studies of the effects of these three variables. The lime dosage usually can be varied at will, but the variation of CSTR residence time and sludge concentration are limited by the reactor volume and settler capacity, respectively. However, on laboratory bench-scale plants all three parameters may be varied indepen-

dently. For this reason a study of these three variables was undertaken on a bench-scale plant.

Lime treatment of secondary effluent was investigated under the following set of test conditions,

(1) pH constant, no sludge inoculation and retention time varied.

(2) Repeated (1) above at 4 different pH values.

(3) A pH identical to the control pH on the full-scale plant was selected and held constant together with constant residence time while the sludge concentration varied.

(4) From the results of (3) above the optimal sludge concentration was selected and held constant and the reactor residence time was varied.

Tests sets (1) and (2) were exploratory to obtain a general idea of the response of the process when no sludge was added. The principal objective was to inquire if retention time plays an important role in the process. These two test sets were made over a range of pH values because lime treatment may have one or more of the following objectives, i.e. P-removal, clarification, preparation for ammonia stripping and magnesium removal, the sequence in general requiring an increasing pH from first to last. With no sludge added the time effect is more evident, for from the literature it is clear that sludge addition speeds up the reaction rates to such a degree that it may mask a time effect in every one of the objectives listed above. Indeed, the attainment of adequate removal may in fact be possible without sludge addition, in which event the complication of sludge recirculation may be avoided. Also, if no sludge is added, flotation separation becomes a possible alternative to gravity separation.

In test set (3) the sludge concentration was varied to establish the effect of different sludge concentrations on precipitation and effluent quality. An attempt was also made to establish the optimum sludge concentration for the selected constant pH and residence time.

The pH selected to be kept constant was pH = 11,2. The choice of this value was influenced by observations already made on the full-scale plant, i.e. the "optimum" lime treatment pH was about 11,2 for achieving the objectives, P-removal, clarification, etc. listed above. A constant residence time of 5 minutes was chosen for this test set based on the results obtained in (1) and (2) above.

Having obtained the optimal sludge concentration in test set (3) the pH of 11,2 and the optimal sludge concentration were kept constant, while the retention time was varied to investigate what is the minimum concomitant time for optimal efficiency (test set 4).

4.1 Bench Scale Plant Description and General Experimental Procedure

A detailed description of the bench-scale plant used in this investigation is given in Chapter 3, Section 4.1. The general procedure for conducting a secondary effluent lime-treatment test run was as follows (refer to schematic flow diagram, Figure 4.8): Secondary effluent (500ℓ) was collected from the Pretoria Sewage Works a day or two before the commencement of the test run. The effluent was stored in glass fibre holding tanks (2 x 250ℓ) from which it was directly pumped to the CSTR during the continuous precipitation experiments. Each run lasted approximately nine hours. Lime used in these experiments was made up as 5 to 10 percent slurries. All the experiments were conducted at 20°C in a constant temperature room. Immediately prior to commencing a run, samples of effluent were drawn from the two holding tanks and analysed for pH, total and dissolved calcium, magnesium, and dissolved ortho-phosphate, total alkalinity, COD, ammonia and nitrate.

A test was commenced by switching on the mechanical stirrers in the effluent holding tanks to ensure a homogeneous solution. Five minutes later the two centrifugal pumps serving the two holding tanks were switched on and the individual flows were set and stabilized by adjusting the needle-valves on the flow meters. Simultaneously, a peristaltic feed pump was switched on to pump a lime slurry from an intensely mixed chemical feed tank (1,0ℓ) to the secondary effluent transporting tube just prior to the CSTR (Figure 4.8). The

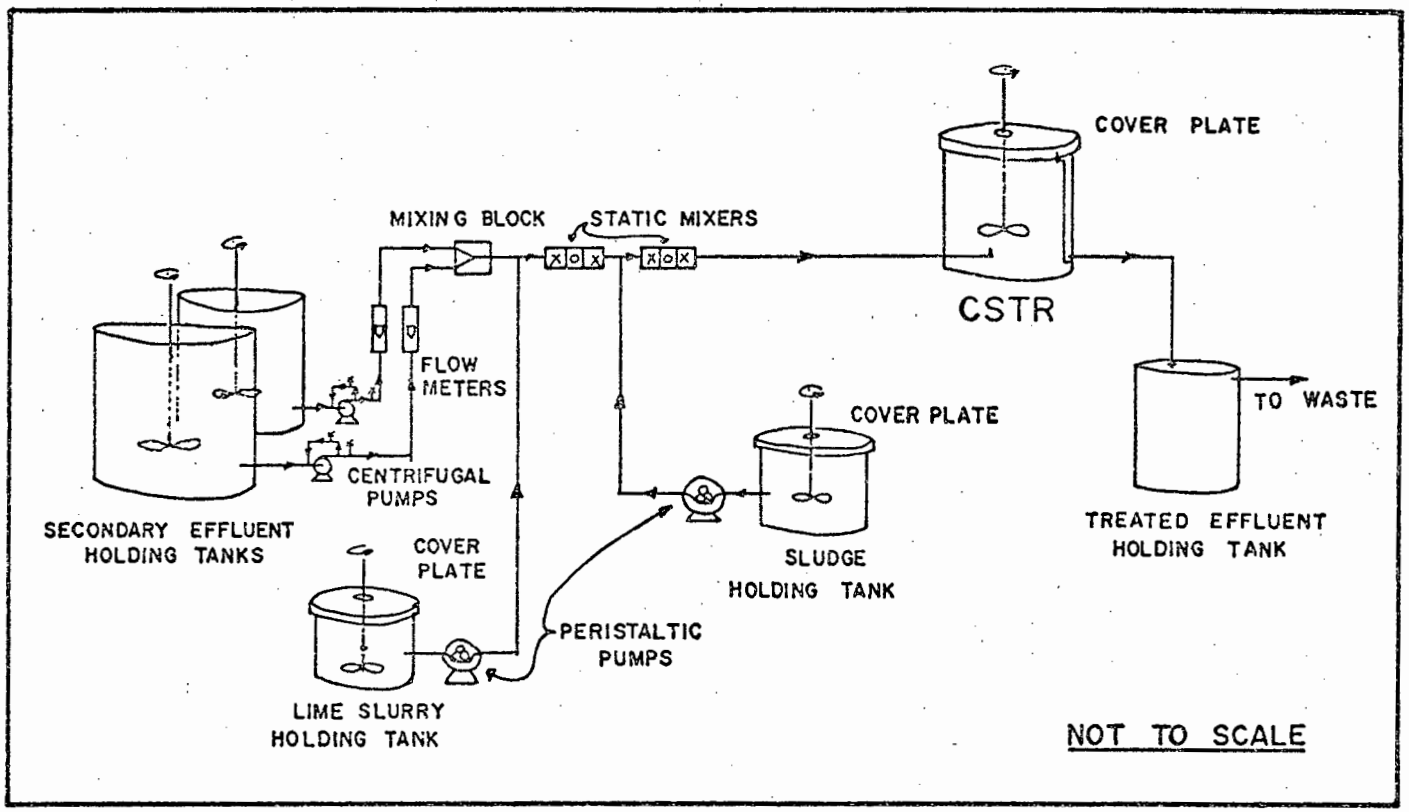

Figure 4.8. Schematic flow diagram of equipment used in bench-scale lime treatment tests

lime-secondary effluent mixture was discharged into a CSTR. The residence time in the reactor was determined by the flow rate of the secondary effluent and the reactor volume (see Chapter 3, Table 3.1). The effluent from the reactor discharged into a treated effluent holding tank from which the overflow discharged to a drain.

pH Electrodes were calibrated with NBS standard buffers. After calibration the electrodes were suspended in the reaction solution from the reactor cover (Figures 3.11 and 3.12). The pH was monitored continuously and recorded on a strip-chart recorder. The lime dosing rate was adjusted to effect a selected reactor solution pH. Constant effluent pH could only be attained by maintaining vigilant control, since the secondary effluent and lime slurry flow rates tended to fluctuate. Samples of reactor effluent were drawn for analysis only after the pH had remained constant for at least three reactor residence times. A second set of samples was drawn after a further one to five residence times had passed. A third set of samples was drawn if the alkalinity of the first two sets did not agree within 5 percent. This completed the run for this set of conditions. Thereupon the experimental conditions were changed, depending on the variable being studied, i.e. the effluent flow was changed to give a different mean residence time; or the lime slurry dosage rate was changed to give a different effluent pH; or the sludge feed rate was altered to give a different sludge concentration in the reaction solution.

Sample taking, preparation and analysis were as follows : Two types of samples were taken. The first as a 150 mℓ sample directly from the reactor effluent stream. It was acidified to a pH of 4 (or lower) to dissolve all acid solubles, vacuum filtered (Whatman No 42) to remove the acid insolubles and analysed for total calcium, magnesium, ortho-phosphate and ammonia. A second 150 mℓ sample was obtained by continuous vacuum filtration of a small side stream flow of the reactor effluent stream. The flow rate of this side stream was very low, approximately 50 mℓ per minute on to an 11 cm diameter filter paper (95 cm^2), ensuring a minimum time lag (<10 to 20 sec) between the

sample leaving the reactor and it being filtered. pH and total alkalinity were immediately determined on a portion of the filtrate. The rest of the filtrate was acidified to pH 4 to quench any further precipitation. The acidified filtrate was analysed for calcium, magnesium, ortho-phosphate, COD and nitrate. These analyses correspond to the residual dissolved concentrations of these parameters for the conditions under which they were obtained.

Raw data collected during this series of tests are listed in Appendix 11.

4.2 Effect of CSTR Residence Time on Lime-Effluent Reactions at Various Constant pH Values, in the Absence of Sludge Addition

In the test sets (1) and (2) five sets of tests were performed, each at a different pH. For each constant pH test the CSTR residence time was varied. No sludge was added to the reactors. The influent to the laboratory-scale plant was secondary treated effluent from a trickling filter plant. The five pH values were chosen as representative of typical pH values which may be encountered in practice in the lime treatment of secondary effluent. The CSTR residence times studied ranged from 1,1 to 14,0 minutes. This range of residence times is also fairly representative of CSTR residence times likely to be encountered in practice.

In addition to the sampling as described in Section 4.1, samples were also drawn from the reactor effluent stream, placed in 1ℓ sealed glass vessels and mechanically agitated for periods of 24 hours or longer, to determine if extended batch reaction times resulted in further effluent stabilization.

Typical results demonstrating the effect of CSTR residence time on the quality of lime-treated secondary effluent, at pH 11,4 and in absence of inoculated sludge, are illustrated in Figures 4.9(a-h). Results obtained for lime treatment to pH values 10,0; 10,5; 11,0 and 11,2 are tabulated in Appendix 11. A discussion of some of the various reactions are given below.

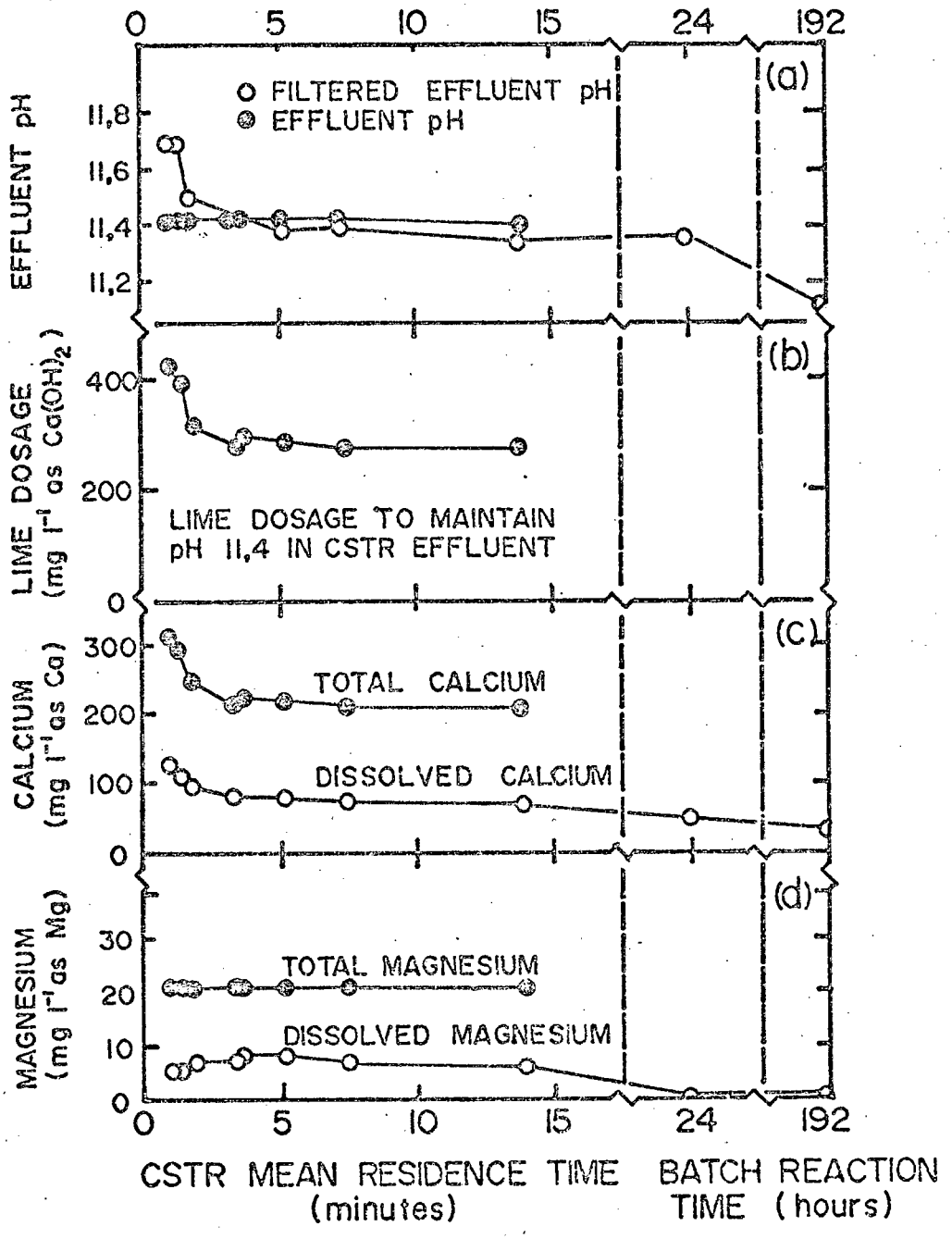

Figure 4.9(a-d). Typical results for CSTR lime-treated secondary effluent (Control pH=11,4)

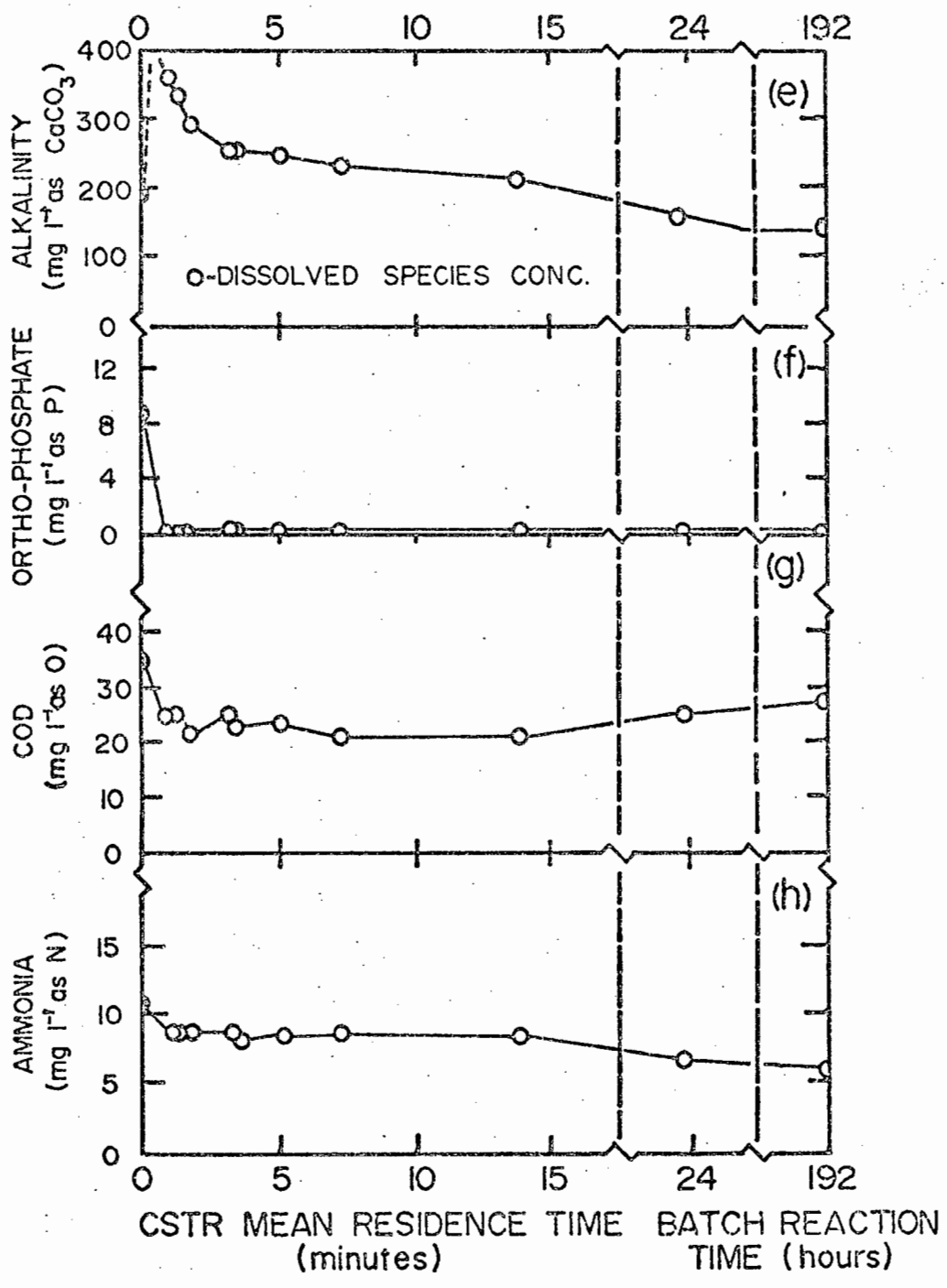

Figure 4.9(e-h). Typical results for CSTR lime-treated secondary effluent (Control pH = 11,4)

Filtered effluent pH

From Figure 4.9(a) it is evident that although the reactor pH was kept constant at 11,4, *filtered* effluent pH values were *not* constant over the range of residence times studied. At short residence times, i.e. less than 3,5 minutes, the filtered effluent pH values were higher than the reactor pH values. At residence times longer than 3,5 minutes, filtered effluent pH values were equal to or slightly lower than the reactor pH values.

The substantial increases in the pH of filtered samples at short mean residence times can only be attributed to lime dissolution during the vacuum filtration process. This hypothesis appears reasonable since lime dissolution is known to be time dependent, e.g. at 2 minutes batch reaction time only approximately 60 percent of the total lime dosage will have dissolved (Figure 4.6). During vacuum filtration the liquid phase of the effluent being filtered has to pass through a mat of solids of undissolved lime and precipitates that have already formed on the filter paper. Further dissolution of the lime particles during this intimate contact period, therefore, is possible.

The slight reduction in pH during filtration of effluent from CSTR's with longer residence times, is a well known phenomenon. It results from the absorption of carbon dioxide from air by alkaline effluents during the filtration process. In supersaturated waters it may also be due to the precipitation of alkaline salts, such as $CaCO_3$ and $Mg(OH)_2$ during contact with the solids mat on the filter paper. Thus during filtration at short retention times the dissolution of lime predominates over the precipitation and at long retention times the precipitation effect predominates over the lime dissolution.

The above observations illustrate one of the fundamental problems associated with all techniques used for quenching chemical reactions involving a phase change - the technique itself may in some way affect the reaction it is quenching. Phase separation by filtra-

tion was the only practical technique available. For this reason limitations of the technique must be considered when the data obtained by this means are interpreted.

Filtered effluent pH values were apparently stabilized at CSTR mean residence times of 5 minutes or longer. However, it is evident from Figures 4.9 (a, b, c, d and e) that during long batch reaction times, i.e. 24-192 hours, further pH reductions due to very slow secondary precipitation phenomena take place. These observations are characteristic of all the test series at the different pH levels, i.e. 10,0 to 11,4 (see Appendix 11).

The secondary precipitation phenomena will be discussed in greater detail in the subsections on residual calcium and magnesium.

Lime Dosage

The lime dosage rate to maintain a constant pH in the CSTR reactor over the range of residence times studied, was not constant (see Figure 4.9(b)). At short residence times, i.e. 1 to 2 minutes, considerably higher lime dosage rates were required than at residence times of 3 minutes or longer. The lime dosage rate stabilized at the longer retention time. This observation may be explained as follows : Due to the time dependence of the lime dissolution reaction, higher lime dosage rates are required at short residence times to achieve the same reactor effluent pH than at longer residence times, as the latter allows time for more complete lime dissolution. Similar observations were made for all the pH values studied (see Appendix 11).

In general it may be concluded that the lime dosage required to effect a desired pH is not only a function of the chemical quality of the influent to be treated, but also the CSTR residence time, particularly for reaction retention times shorter than 3 minutes. The lime dosage to attain a particular pH decreases as the retention time increases.

Residual Calcium

Residual total dissolved calcium concentrations, Ca_T^{2+}, as a function of mean residence times, R, are shown in Figures 4.9(a) and 4.10. The Ca_T^{2+} versus R relationships are indicative of the progression with time of all the lime-secondary effluent reactions involving calcium species. These include $Ca(OH)_2$ dissolution and $CaCO_3$ and $Ca_3(PO_4)_2$ precipitation.

From Figure 4.10 it is evident that calcium removal takes place in two phases, a rapid primary phase and a slow secondary phase. The primary phase is complete within less than 2 minutes at all the pH values. The secondary phase is not complete even at 14 minutes, the longest CSTR residence time studied. The secondary phase appears to be pH dependent, i.e. at high pH values significant additional precipitation took place, e.g. 30 mg ℓ^{-1} (as Ca) at pH 11,4, whereas only an additional 3 mg ℓ^{-1} (as Ca) precipitated at pH 10,0.

Secondary phase precipitation continues for very long periods. With reference to Figure 4.11 (b), samples held for 24 hours showed reductions in residual calcium of 20 to 30 mg ℓ^{-1} (as Ca). This effect was evident for all the pH values studied.

Residual Magnesium

Residual total dissolved magnesium concentrations as a function of CSTR mean residence time, for five pH values, is illustrated in Figure 4.12 and for one residence time (5 min) for different pH values in Figure 4.13. It is evident from Figures 4.12 and 4.13 that magnesium removal is primarily a function of pH. Magnesium removal at pH values below 11,0 is low, but increases rapidly with increasing pH values above 11,0. Figure 4.12 also indicates that there is rapid primary magnesium removal which is complete within 1 to 2 minutes, but thereafter there is a slow secondary phase which continues even at long batch reaction times, i.e. 24 hours or longer (see Figures 4.9(d) and 4.11(c)).

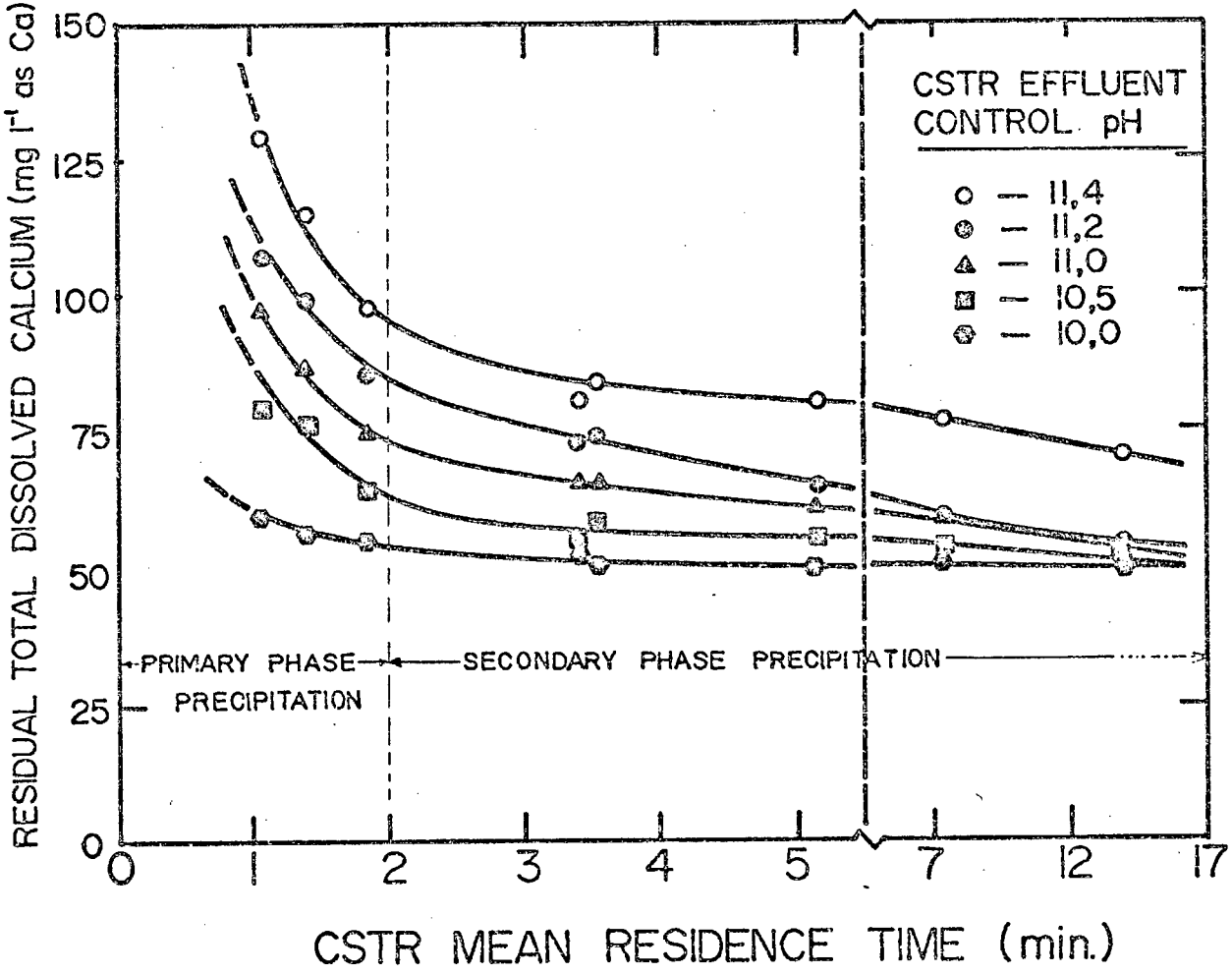

Figure 4.10. Residual calcium concentration as a function of CSTR mean residence time for lime-treated secondary effluent

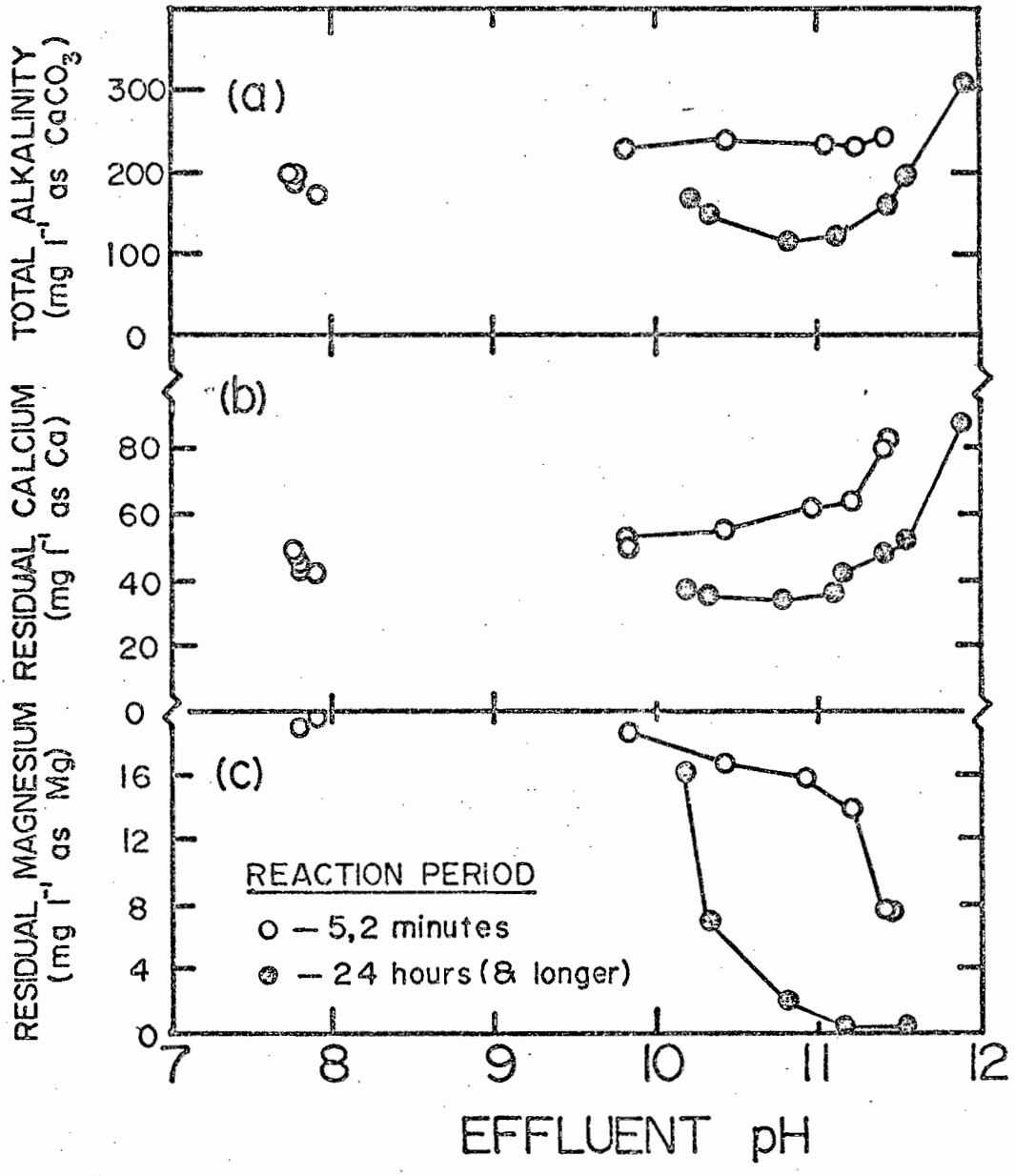

Figure 4.11 (a-c). Ca_T^{2+}, Mg_T^{2+} and Alkalinity residual values for lime-treated secondary effluent, for two reaction periods

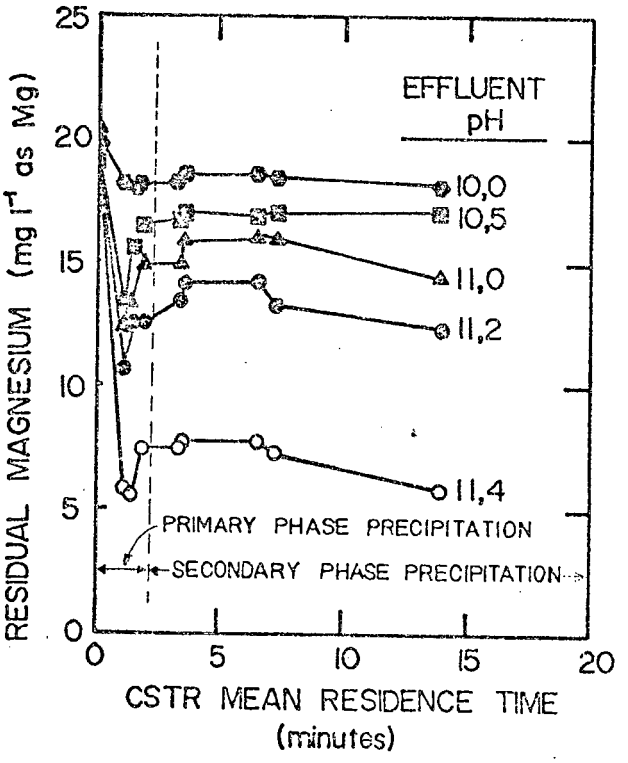

Figure 4.12. Effect of residence time on residual magnesium concentration in lime-treated secondary effluent from CSTR systems

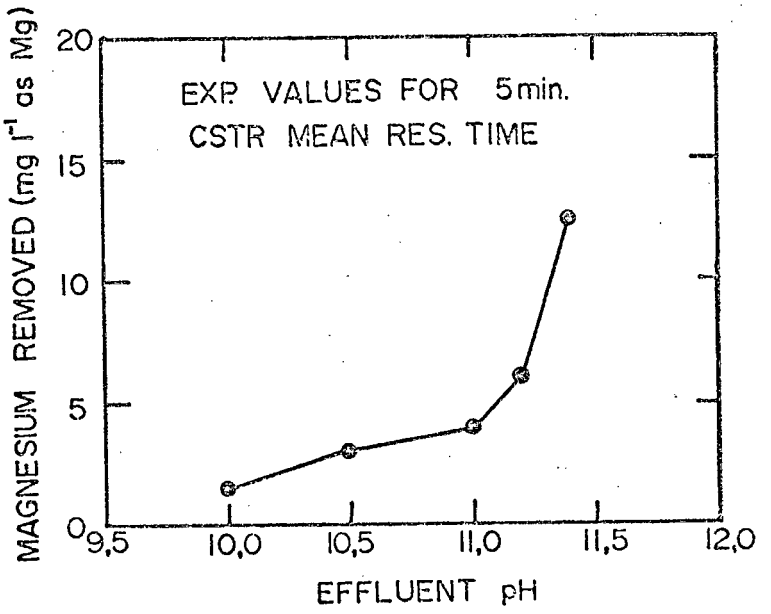

Figure 4.13. Effect of pH on magnesium removal from lime-treated secondary effluent in a CSTR system (for 5 minutes mean residence time)

Liu and Nancollas (1973) in their study of pure system magnesium hydroxide precipitation made similar observations to those reported above. They concluded that in batch tests, initially magnesium hydroxide precipitates rapidly, followed by slower precipitation and possibly recrystallization, requiring extended reaction periods.

Ortho-Phosphate

Ortho-phosphate removal at pH 11,4 (Figure 4.9(f)) appears to be almost instantaneous, since no dissolved ortho-phosphate residuals could be measured in the lime-treated secondary effluents even at the shortest CSTR residence time studied. Similarly, complete ortho-phosphate removal, i.e. PO_4-residuals less than 0,1 mg ℓ^{-1} (as P) at the shortest CSTR residence time studied, was measured for the pH range 10,5 - 11,2 (Table 4.4). A slight residual of 0,3 mg ℓ^{-1} (as P) was measured at pH 10,0.

In general it may be concluded that ortho-phosphate removal from lime-treated secondary effluent is complete at pH values of 10,5 and higher, and CSTR residence times longer than 1,1 minutes.

Table 4.4

Removal of PO_4, COD and NH_3 from secondary effluent at different pH values in a CSTR with a mean residence time of 1,07 minutes

Reactor pH	10,0	10,5	11,0	11,2	11,4
PO_4-P (sec. eff.)	7,8	6,8	8,0	6,0	8,7
PO_4-P (reactor eff.)	0,3	<0,1	<0,1	<0,1	<0,1
COD (sec. eff.)	33	28	31	-	35
COD (reactor eff.)	26	25	28	24	24
NH_3-N (sec. eff.)	7,8	12,0	11,3	8,1	10,9
NH_3-N (reactor eff.)	5,0	9,6	9,0	6,7	8,4

Chemical Oxygen Demand

Partial removal of dissolved Chemical Oxygen Demand (COD) also appeared to be almost instantaneous (Figure 4.9(g)), since residual dissolved COD concentrations stabilized from the shortest mean residence time (1,1 minutes) measured. Similar observations were made at all the pH values studied (see Table 4.4 and Appendix 11). Removal of dissolved COD did not appear to be related to pH for the range of pH values investigated, i.e. 10,0 to 11,4.

Ammonia

Partial removal of ammonia also appeared to be nearly instantaneous (Figure 4.9(h)), since residual ammonia concentrations stabilized from the shortest mean residence time (1,1 min.) studied. Similar observations were made at all the pH values studied (Appendix 11). As in the case of partial COD removal, partial ammonia removal did not appear to be related to pH in the range of pH values investigated, i.e. 10,0 - 11,4. It is clear that lime addition to secondary effluent results in the conversion of NH_4^+ to NH_4OH and NH_3, but the mechanism of partial ammonia removal from mildly agitated CSTR solutions is not understood. Ammonia removal may be due to air stripping of NH_3, the formation of magnesium ammonium phosphate or possibly an inherent error in the analytical technique used for determining ammonia.

Scale Formation

Even though the experiments were run without seed sludge addition, scale formation on reactor walls, impellers, transport tubing and pH electrodes was negligible. This observation contrasts strongly with the severe scale formation observed in CSTR experiments for pure calcium carbonate precipitation, where significant quantities of scale formed within an hour or two of initiating an experimental run. It would appear that the co-precipitation of $CaCO_3$, $Ca_3(PO_4)_2$ and $Mg(OH)_2$ in the presence of other heterogeneous substances, such as dissolved and suspended organic material, results in a mobile non-adherent sludge rather than scale.

4.3 Effect of Sludge Concentration at Constant pH and Constant Residence Time

In the previous section the effects of residence time and pH were studied for lime treatment of seconary effluent in the absence of inoculated seed sludge. In this section the effect of the sludge concentration on the lime-secondary effluent reactions is reported, for constant pH and residence time. The constant pH value selected was 11,2, primarily because this was the pH value utilized on the full-scale plant. It was also expected that the beneficial effect of sludge recirculation on magnesium removal at this particular pH value would be considerable, since magnesium removal in the absence of sludge was poor at short residence times, but good at long batch reaction times (Figure 4.12(c)). A constant residence time of 5 minutes was chosen, since relatively stable lime-treated secondary effluent is produced at residence times of 5 minutes or longer (Figure 4.9 (a, b, c, d)).

The laboratory bench-scale plant (Figure 4.8) and the operational procedures used for this test run were as described previously (section 4.1), the only change being that sludge from a reservoir tank was inoculated into the waste stream, whereas previously no sludge was added. Sludge was inoculated to give reactor inoculated sludge concentrations ranging from 0 to 15 000 mg ℓ^{-1}.

Two points of sludge addition to the waste stream were studied, i.e. prior and subsequent to the point of lime slurry addition to the waste stream. Each of the added streams, i.e. lime slurry and sludge, was mixed into the waste stream by means of a six segment static mixer (see Figure 4.8). The mixture then discharged into a precipitation reactor. The precipitation efficiency of the system was evaluated by measuring residual total dissolved calcium and magnesium in the effluent from the reactor. The effluent was vacuum filtered rapidly and the filtrate acidified to quench any further precipitation prior to the determination of calcium and magnesium.

The effect of sludge inoculation on reactor effluent residual total dissolved calcium, Ca_T^{2+}, is illustrated in Figure 4.14. When no

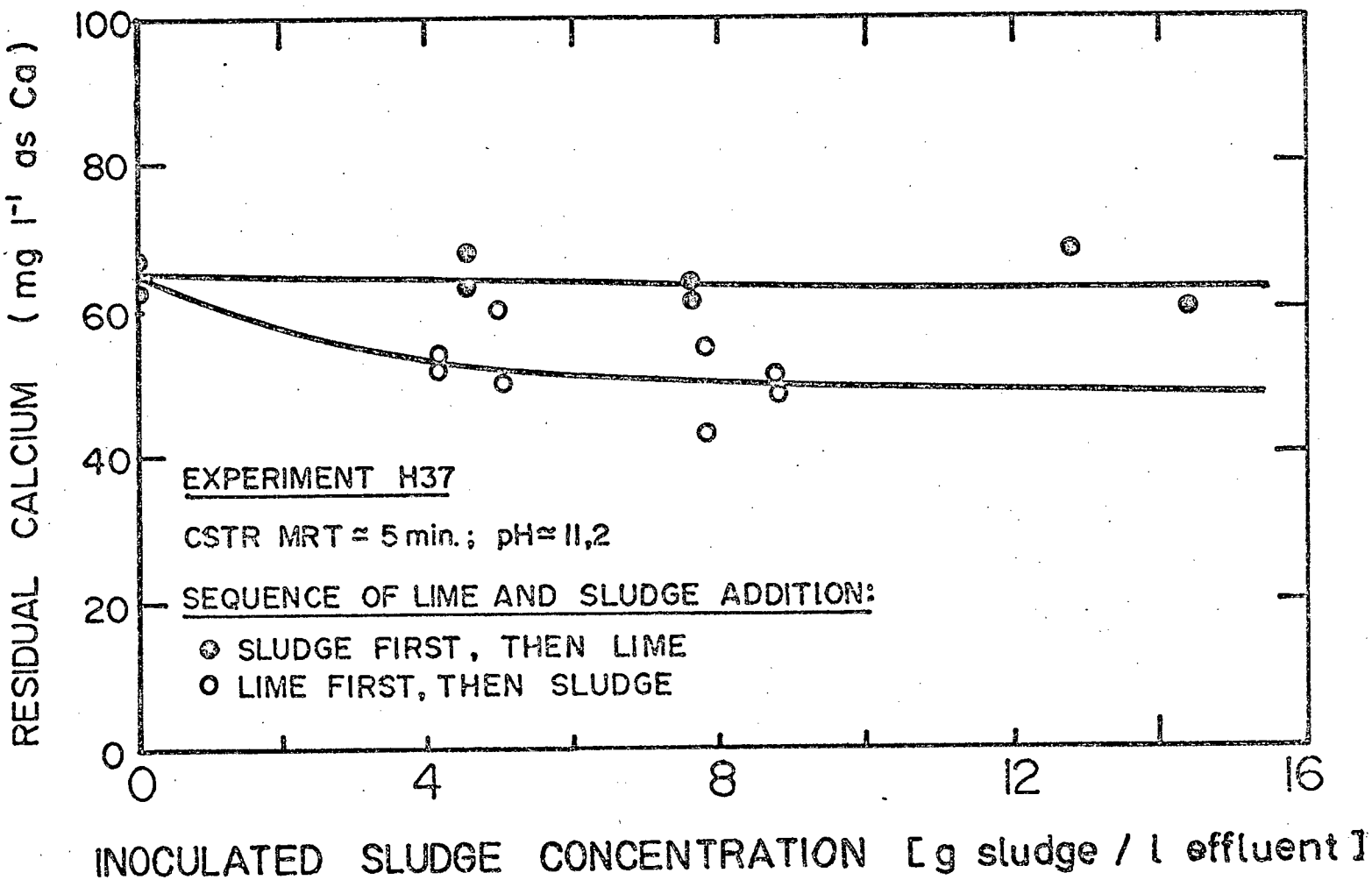

Figure 4.14. Effect of inoculated sludge concentration on calcium removal in a CSTR system

sludge was inoculated, the Ca_T^{2+} concentration was approximately 65 mg ℓ^{-1}(as Ca). When sludge was inoculated subsequent to the lime addition point, significantly improved calcium removal resulted, i.e. the Ca_T^{2+} concentration dropped to approximately 50 mg ℓ^{-1}(as Ca). If the effect of sludge on Ca_T^{2+} at pH 11,2 is compared with the effect of an extended batch reaction period (24 hours) on Ca_T^{2+}, i.e. a reduction of 65 to 50 mg ℓ^{-1} (as Ca) as compared to 65 to 45 mg ℓ^{-1}(As Ca), respectively (compare Figures 4.14 and 4.11(b)), it is clear that *reaction time and sludge inoculation (10 000 mg ℓ^{-1}) have similar effects.* However, whereas reaction times of 24 hours or longer are not feasible in practice, recirculation of sludge to effect concentrations of 10 000 mg ℓ^{-1} in a reaction system is feasible. Sludge recirculation is therefore indicated as a practical means of overcoming the problem of slow secondary calcium removal reactions.

When sludge was inoculated prior to the lime addition point, no significant improvements in the residual calcium were observed, compared to the effluent from reactors with no sludge addition. This phenomenon is thought to be due to the inhibiting effect of sludge on lime dissolution (see review of paper by Jenkins and Lee, 1976, Chapter 2, Section 5.2).

The effect of sludge inoculation on reactor effluent residual total dissolved magnesium, Mg_T^{2+}, is illustrated in Figure 4.15. When no sludge was inoculated the Mg_T^{2+} concentration was 16 mg ℓ^{-1}(as Mg). When sludge was inoculated, both prior to and subsequent to the point of lime slurry addition, magnesium removal improved significantly. The Mg_T^{2+} concentration decreased as the sludge concentration increased, to a minimum value of 6 mg ℓ^{-1}(as Mg) at sludge concentrations of 10 000 mg ℓ^{-1} or greater. The improved magnesium removal is attributed to the additional surface area provided for precipitation by the high concentrations of $Mg(OH)_2$ seed present in the inoculated sludge, i.e. approximately 1000 mg ℓ^{-1} in a sludge of 13 000 mg ℓ^{-1}.

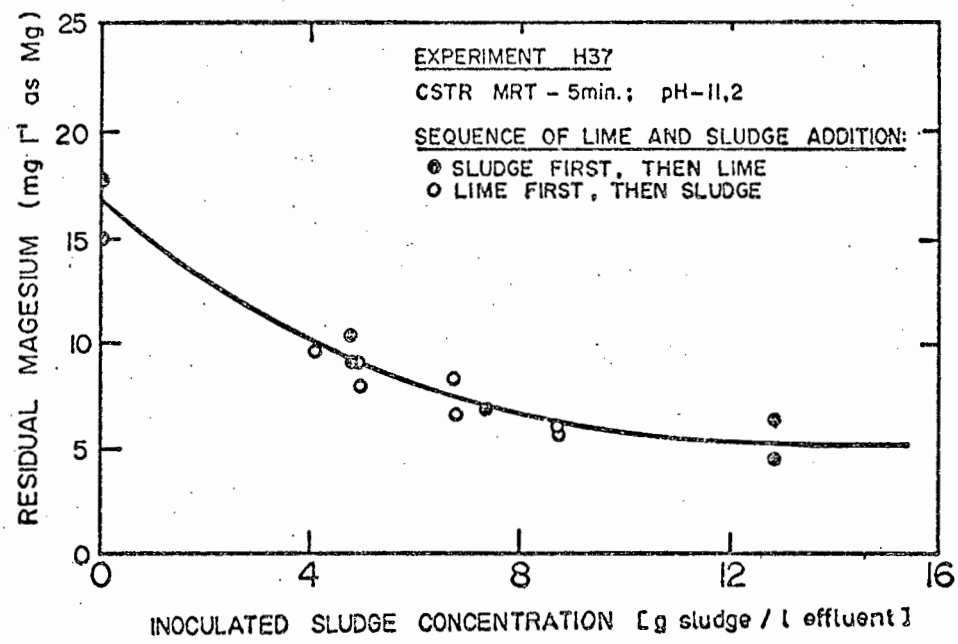

Figure 4.15. Effect of inoculated sludge concentration on magnesium removal in a CSTR system

The effect of sludge on improving magnesium removal at pH 11,2 is similar to the effect of extended batch reaction time when no sludge is inoculated into the reaction system (compare Figures 4.12(b) and 4.15). Therefore, as in the case of improved calcium removal, sludge recirculation is indicated as the practical means of overcoming the problem of slow secondary magnesium hydroxide precipitation.

From this series of tests (at pH 11,2 and 5 minutes CSTR residence time) it appears that the recommendable sludge concentration for optimal calcium and magnesium removal is about 10 000 mg ℓ^{-1} (see Figures 4.14 and 4.15) which in practice is approximately equivalent to 10-15% clarifier underflow sludge recirculation.

4.4 Effect of CSTR Residence Time at Constant pH and Optimal Sludge Concentration

Once the optimum sludge concentration (10 000 mg ℓ^{-1}) for the lime treatment of secondary effluent at pH 11,2 for the set reactor residence time of 5 minutes was determined, the effect of CSTR residence time was

studied maintaining the pH at 11,2 and the sludge concentration near the optimum value. The results are listed in Table 4.5. It is evident from the Ca_T^{2+} values at the three different residence times that sludge inoculation (13 000 mg ℓ^{-1}) resulted in stabilized Ca_T^{2+} values even at residence times as short as 1,1 minutes. In the absence of inoculated sludge the Ca_T^{2+} concentrations reduced from 70 to 64 mg ℓ^{-1} (as Ca) when increasing the residence time from 1,1 to 5,0 minutes, whereas in the presence of sludge the residual calcium concentration was 38 mg ℓ^{-1} (as Ca) even at only 1,1 minutes residence time. Reactor effluent residual magnesium values, even in the presence of inoculated sludge, were not completely stabilized, since on increasing the mean residence time from 1,1 to 5,0 minutes, a further 0,5 mg ℓ^{-1} (as Mg) reduction in Mg_T^{2+} took place.

Table 4.5

Effects of CSTR residence time and both the absence and presence of inoculated seed sludge on the concentration of residual calcium and magnesium in lime-treated secondary effluent

Mean Residence Time (min)	Residual Total Dissolved Calcium (mg ℓ^{-1} as Ca)		Residual Total Dissiolved Magnesium (mg ℓ^{-1} as Mg)	
	without sludge	with sludge	without sludge	with sludge
1,1	70	38	14,0	4,8
1,7	68	38	13,0	4,6
5,0	64	38	13,8	4,3
After a further 24 hours batch reaction	45	-	1,0	-

Comparing the residual calcium and magnesium concentrations listed in Table 4.5 for effluent samples without sludge held for 24 hours, with samples with sludge reacted for only 1 to 5 minutes CSTR residence time, it is clear that the qualities are approximately the same. It is concluded that sludge addition of 13 000 mg ℓ^{-1} and 1 to 5 minutes retention time give approximately the same effluent quality as 24 hours batch reaction time in the absence of added sludge. This comparison is qualitative only. No tests were perfomed on samples without seed sludge, which were held for longer than $1\frac{1}{2}$ hours (see Section 3) but shorter than 24 hours. Therefore, it is not possible now, to determine accurately the minimum batch time that will give a stable effluent. However, it is clear that sludge addition will decrease the CSTR residence time by at least an order of magnitude.

4.5 Kinetics of Lime-Effluent Reactions

Prerequisites for studying the kinetics of reactions in complex systems in which more than one reaction takes place, are

(1) a knowledge of all the reactions taking place over the range of conditions studied, and
(2) a knowledge of the time behaviour of all the reactants or products.

When lime is added to secondary effluent at least eleven simultaneous reactions take place (Eqs. 4.1 to 4.11). To study the kinetics of all these reactions requires measurements of the changes in concentration with time of all the reactants or products. Since quantitative or even qualitative measurement of the changes in concentration with time of the solid species was not possible, only the changes in dissolved species concentrations with time were monitored, as reported in Section 4.4. The results showed that two phases of calcium and magnesium removal from solution were evident - a primary phase of rapid precipitation and a secondary phase requiring very long periods for achieving stable effluents.

This two stage behaviour makes the formulation of the kinetics very unreliable and difficult. However, it is doubtful whether there is much merit in pursuing the kinetic approach *per se*, for with sludge addition the reactions are completed in such a short space of time that there is no limitation imposed on the process by the kinetic behaviour. Stable or near stable effluents can be produced by simple practical procedures.

4.6 Conclusions

(1) Reactions in the absence of inoculated sludge

(a) Calcium removal from lime-treated secondary effluent takes place in two phases, rapid primary precipitation resulting in 80 to 90 percent reaction completion within 2 to 3 minutes CSTR residence time, and slow secondary precipitation requiring very long residence times to produce effluents stable with respect to calcium.

(b) Magnesium removal from lime-treated seconary effluent is primarily a function of pH. As in the case for calcium removal, two phases of precipitation were observed, a rapid primary phase and a slow secondary phase.

(c) Batch reaction times of 24 hours and longer are necessary for producing effluents stable with respect to Ca_T^{2+} and Mg_T^{2+}.

(2) Reactions in the presence of inoculated sludge

(a) Sludge inoculation into the lime-secondary effluent reaction system, at concentrations of 10 000 mg ℓ^{-1} or higher, resulted in stable effluents at short CSTR residence times of 1 to 2 minutes.

(b) It is evident that the main problem associated with lime treatment of secondary effluent is incomplete calcium carbonate and magnesium hydroxide precipitation due to the slow secondary precipitation phases. This problem may be minimized by sludge inoculation into reaction systems, whether or not conventional sedimentation or

flotation units are used for solids separation. Lime treatment processes which do not make use of sludge recirculation to the precipitation vessel (or zone), will give rise to unstable clarified waters. It is clear that extended precipitation opportunity needs to be provided if stable effluents are to be produced and here the simplest solution is recirculation of high concentrations of sludge. The favourable effect of sludge contact with the effluent can be further enhanced by utilizing sludge blanket clarifiers, a proposal further considered in Chapter 5.

5. CHARACTERIZATION OF LIME-TREATED EFFLUENTS

In the previous section the kinetic behaviour of various inorganic reactions in a lime-secondary effluent system was investigated. It was shown that these reactions are crucially affected by sludge addition to the system and that from a practical point of view near stable effluents can be produced only by sludge recirculation. Although it was not possible to formulate the kinetics of the precipitation reactions, the procedures to be adopted to obtain near stable effluents could be delineated fairly conclusively.

From a design point of view a major unresolved problem is the prediction of final stable states. In contrast with the previous problem, we are now concerned with a steady state condition, a "near equilibrium" problem, i.e. what will be the final condition of a water for different chemical additions accepting that the conditions for producing stable effluents are satisfied? Is it possible by means of some simple testing procedure to predict the final states over a range of chemical additions?

Merrill and Jorden (1975) have suggested that it is possible to characterize the behaviour of lime-treated waste water. For this purpose they employed equilibrium theory, substituting "activity product constants" specific to the system being studied for thermodynamic equilibrium constants. They tested their hypothesis on data from a bench-scale plant lime-treating raw sewage.

Their plant had four series reactors in which the lime raw sewage reactions took place in the absence of sludge addition.

It was assumed that if the liquid phase achieved an apparent stable value, as monitored after each of the four reactors, a stable effluent had been produced. They concluded that stable conditions were achieved after 30 minutes total retention time, in all cases they investigated.

The work reported in the previous section casts some doubts on the conclusion of Merrill and Jorden that equilibrium is attained after 30 minutes in the absence of sludge. It was shown that secondary precipitation phenomena are evident in samples kept for longer than 30 minutes. Furthermore, the prediction of stable effluent quality by the Merrill and Jorden model is a complex procedure requiring complete analysis* of the raw and treated water and extensive computer computations. If their model is to be utilized for design purposes, fairly sophisticated analytical and computer facilities are a prerequisite.

Loewenthal and Marais (1976) developed the Modified Diagram of Caldwell and Lawrence (1953) to provide a method for obtaining solutions to equilibrium problems involving the calcium-magnesium-carbonic-water system. This technique requires analysis for only the calcium, magnesium, total alkalinity, pH, temperature and total dissolved solids of the raw water. The Diagram neglects ion pairing and sequestring effects. It has been used successfully for predicting chemical changes in surface and ground waters with chemical dosing. Loewenthal and Marais warn that the Diagram should not be used on effluents from waste water treatment plants as these contain phosphorous and organic matter which appear to influence the thermodynamic solubility product constants of the precipitating minerals. However, they gave no information in what fashion these constants may be affected.

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*Calcium, magnesium, total alkalinity, pH, temperature, total dissolved solids, sulphate, chloride, phosphates (ortho- and organic), ammonia, organic nitrogen, etc.

The work of Merrill and Jorden (1974) indicates that the apparent solubility products of both $CaCO_3$ and $Mg(OH)_2$ for lime-treated waste waters are several orders of magnitude greater than the values for the pure synthetic system. It was therefore decided to investigate if the Modified Caldwell-Lawrence Diagram using increased solubility products can describe the equilibrium or near equilibrium states achieved in the lime treatment of secondary effluents. If this approach gives acceptable predictions it will have practical advantages over the approach of Merrill and Jorden, for the response of a water to different chemical additions can be rapidly estimated without recourse to extensive analyses and time consuming computations.

In attempting to utilize the Diagram cognizance must be taken of experience reported earlier, i.e. equilibrium conditions are attained only slowly and it may not be practical to attempt to attain true equilibrium conditions in experimental investigations for the purpose of design. Therefore, it is necessary to investigate the conditions necessary in laboratory batch tests which will ensure reasonable concurrence between these tests and full-scale plant results. A practical approach would be to define the conditions under which the full-scale treatment is operated and then commence a batch test investigation using analytical grade chemicals. The divergence between experimental results and those predicted by the Diagram incorporating the standard mineral solubility products will give a measure of the error involved. The test conditions can thereupon be changed until an acceptable correlation is obtained. Thereafter these conditions can be used in the chemical conditioning of effluents and by trial and error the Modified Caldwell-Lawrence Diagram with a psuedo $CaCO_3$ solubility product giving an acceptable correlation can be identified. The predictions from this Diagram can then be tested against the results obtained on full-scale plants.

5.1 General Experimental Method

Synthetic samples, secondary effluent and settled sewage were treated in a series of laboratory batch experiments in order to characterize their response to lime treatment.

The synthetic sample was made up from distilled water and analytical reagent grade $CaCl_2$, $NaHCO_3$, NaOH and $MgCl_2$. Synthetic sludge was prepared by precipitating $Mg(OH)_2$ *in situ* and adding analytical reagent grade calcium carbonate to make up a slurry with a $CaCO_3$:$Mg(OH)_2$ ratio of 10:1, i.e. a ratio similar to that of the lime sludges produced on the Stander Plant. The synthetic sludge was washed with copious quantities of distilled water (7 individual batch washings with 3 to 4 times the volume of the thickened sludge), in an attempt to remove or minimize contamination due to liquid phase components and soluble solid phase components in the origional sludge. However, it was not possible to reduce the pH value of the synthetic sludge to a pH value of approximately 8, the pH of the synthetic sample used in this test. The lowest sludge pH value which was attained was 10,27. The inability to reduce the sludge pH to a low value is due to the dissolution of magnesium hydroxide in the distilled water used for washing the sludge (see later, Table 4.7).

In the tests on secondary effluent and settled sewage, samples were drawn from the relevant waste water streams at the Pretoria Sewage Works just prior to the commencement of each experiment. Lime sludge from the Stander plant's primary clarifier was drawn at the same time for use in the experiments with these two effluents. The sludge from the Stander Plant was washed with copious quantities of secondary effluent and settled sewage. Here again it was not possible to reduce the pH value to 8, i.e. the approximate pH value of these two effluents. In the case of secondary effluent washing the sludge pH reduced to 9,6 and in the case of settled sewage washing the sludge pH reduced to 10,0.

An experiment was commenced by placing approximately 21ℓ effluent in a 22,5 ℓ glass reaction vessel. This vessel was sealed almost completely from the atmosphere to eliminate or minimize carbon dioxide absorption by the lime-treated effluent (Figure 4.16). A sample of this raw effluent was analyzed for : pH, alkalinity, calcium, magnesium, ortho-phosphate, COD and ammonia.* Approximately 1,5ℓ sludge was added to the effluent and the resultant mixture was stirred for 15 minutes. Vigorous mixing, ensuring adequate sludge dispersion throughout the reactor, was effected by means of a three blade stainless steel stirrer (± 500 r.p.m.). After the 15 minutes stirring period a sample of the effluent-sludge mixture was withdrawn from the batch reactor, the pH determined, suspended solids removed by vacuum filtration and the abovementioned seven parameters were determined on the filtrate.

A series of lime additions were made to the effluent in the batch reactor, increasing the pH in steps of approximately 0,2 to 0,3 of a pH unit at a time, upto a pH of 11,6. For this purpose powdered lime was accurately weighed before each addition. The lime was washed into the reactor using raw effluent. The volume of the reaction solution was kept constant at 22,5 ℓ, i.e. for each sample of treated effluent withdrawn from the batch reactor (± 225 mℓs or 1,0 percent of the total volume) an identical volume of raw effluent was used to wash in the next addition of lime. After each addition of lime a reaction period of 15 minutes was allowed before withdrawing the next sample for analysis from the batch reactor.

The percentage active $Ca(OH)_2$ in the commercial and analytical reagent grade limes used in these experiments was determined by means of the "Sugar Method" (SABS, 1955).

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* Analysis for the latter five parameters was performed on vacuum filtered samples which were acidified to pH 4,0, with 1,0N H_2SO_4

A - 22,5 ℓ GLASS REACTION VESSEL
B - REACTION MIX, FILLED TO NECK OF VESSEL
C - STAINLESS STEEL STIRRING ROD WITH BLADES
D - 500 rpm ELECTRIC MOTOR DRIVE
E - RUBBER BUNG
F - GLASS FUNNEL
G - VENTING SPACE
H - SAMPLE TAP

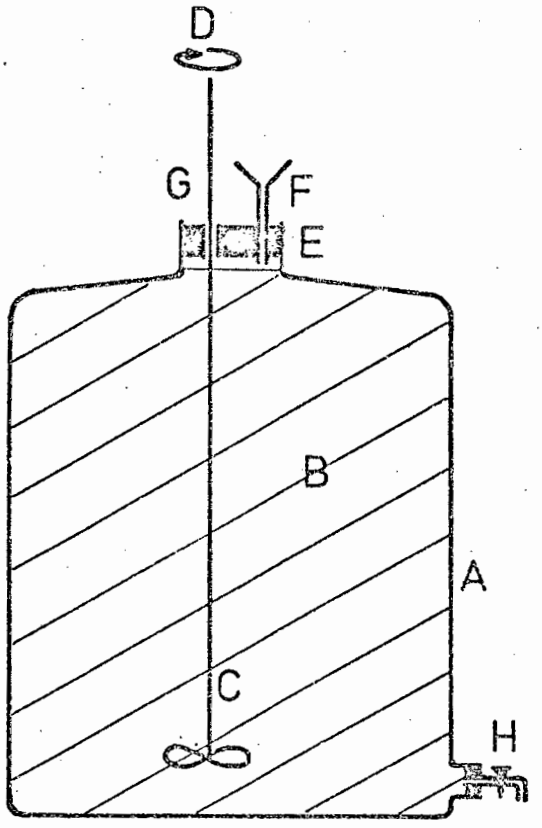


Figure 4.16. Batch reaction vessel used in experiments for effluent characterization

5.2 Synthetic System : $CaCO_3$ - $Mg(OH)_2$

Typical results for the synthetic system experiment are listed in Table 4.6. The experimentally determined relationships between pH and lime dosage, total alkalinity, residual total dissolved calcium and magnesium are illustrated in Figure 4.17(a-d). These

Table 4.6

Typical experimental results for synthetic solution batch lime treatment

Lime Dosage	Reactor Effluent pH	Filtered Effluent pH	Total Alkalinity	Total Dissolved Calcium	Total Dissolved Magnesium
(Effluent only)	8,58	8,66	199	103	115
(Effluent & Sludge	10,17	10,08	217	10	218
13	10,18	10,01	209	10	214
38	10,23	10,13	194	13	194
75	10,28	10,18	166	13	165
113	10,32	10,19	138	15	136
150	10,42	10,27	107	15	111
187	10,50	10,32	79	15	82
212	10,56	10,36	64	18	62
240	10,64	10,46	47	23	45
266	10,76	10,55	45	35	29
293	10,93	10,78	50	48	16
319	11,10	10,96	70	65	8
343	11,20	11,11	85	88	< 8
381	11,36	11,28	115	120	< 8
429	11,51	11,45	156	163	< 8
482	11,64	11,57	205	223	< 8

All parameters, excepting pH, are given in mg ℓ^{-1} (as $CaCO_3$).
Analar lime used in experiment contained 95,9% active $Ca(OH)_2$.

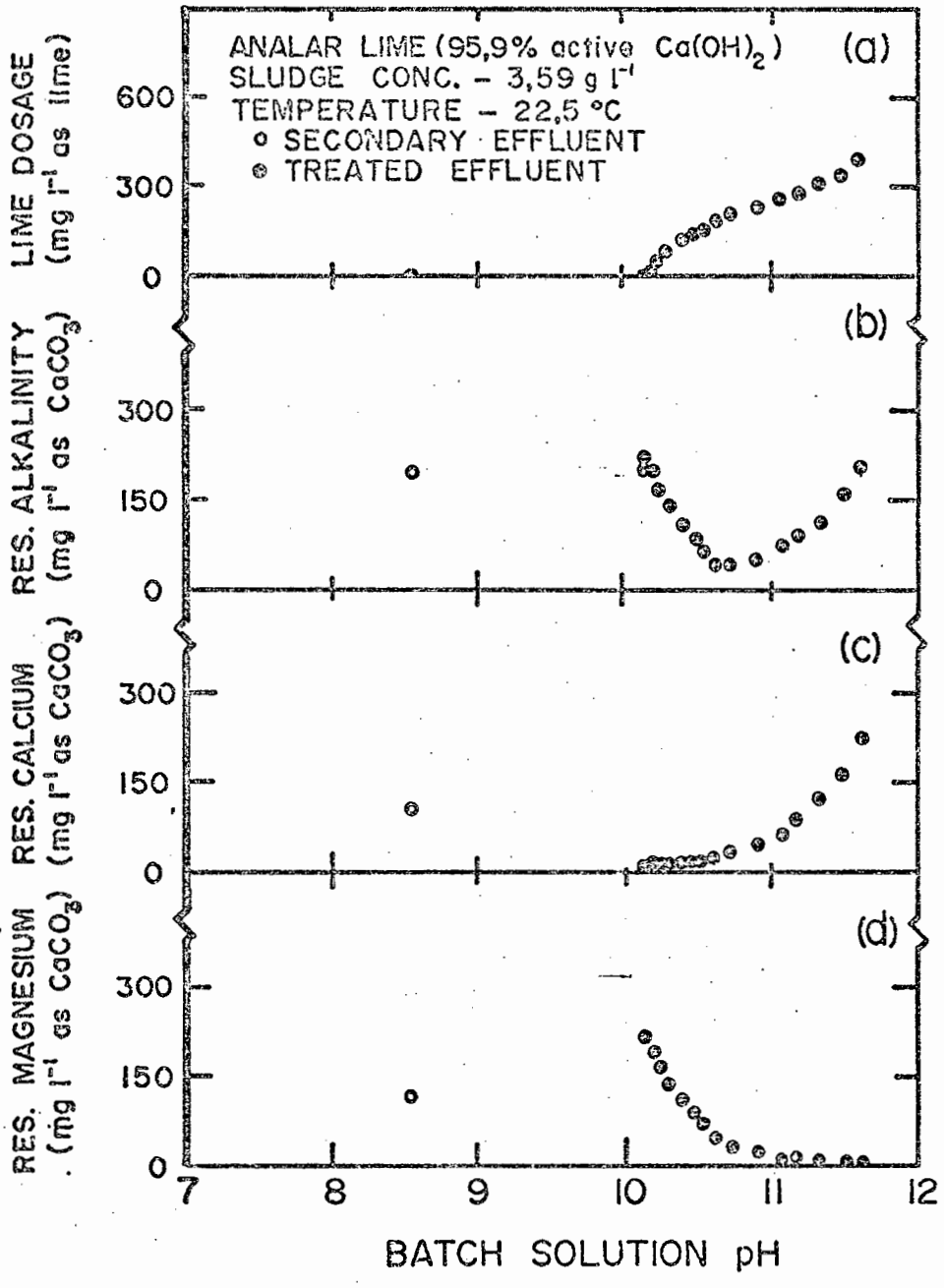


Figure 4.17(a-d). Plots indicating the response of synthetic secondary effluent to lime treatment in the presence of synthetic sludge (batch test)

plots characterize the response of this particular synthetic sample to lime treatment. From the data listed in Table 4.6 other useful information may be estimated, such as the masses of $CaCO_3$ and $Mg(OH)_2$ precipitated for each lime dosage, and hence the relationship between pH and sludge generated can be determined (see Figure 4.18).

In this particular experiment the synthetic sample resembled Pretoria Sewage Works secondary effluent, i.e. similar concentrations of calcium, magnesium and alkalinity (see Table 4.10). However, on addition of the synthetic $CaCO_3$-$Mg(OH)_2$ sludge to the synthetic sample, before the addition of lime, the dissolved calcium and magnesium values changed significantly, i.e. the residual total dissolved calcium reduced from 103 to 10 mg ℓ^{-1} (as $CaCO_3$) and the residual total dissolved magnesium increased from 115 to 218 mg ℓ^{-1} (as $CaCO_3$). This behaviour contrasts sharply with the behaviour when sludge from the full-scale plant was added to secondary effluent, i.e. the residual total dissolved calcium and magnesium remained practically unchanged (see Table 4.7). It is not

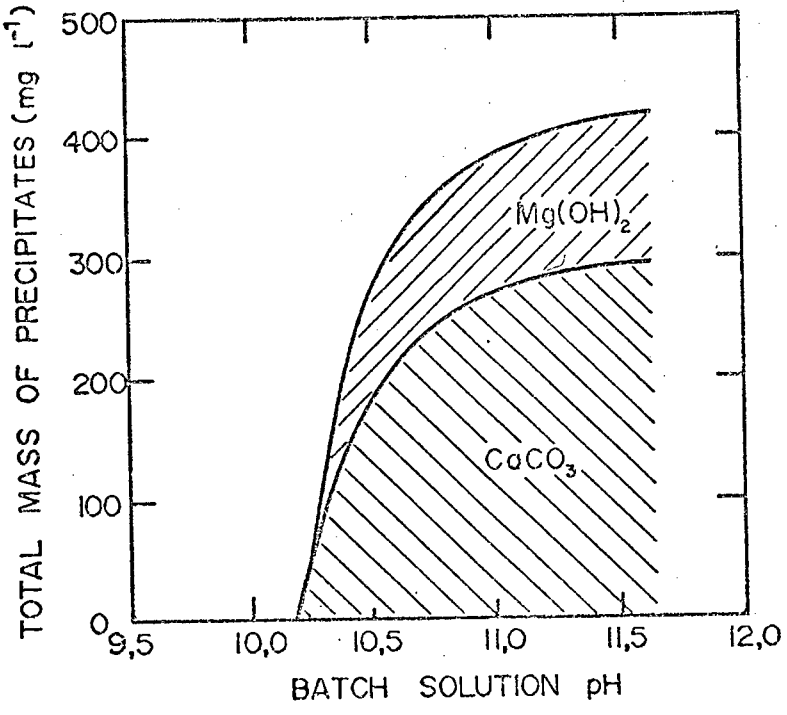


Figure 4.18. Concentration of sludge generated as a function of pH for lime-treated synthetic secondary effluent

Table 4.7

Changes in effluent quality effected by the addition of sludge (before lime addition)

Parameter	Secondary Effluent		Synthetic Effluent	
	Without Sludge	With Sludge	Without Sludge	With Sludge
Calcium (as $CaCO_3$)	103	95	103	10
Magnesium (as $CaCO_3$)	91	99	115	218
Alkalinity (as $CaCO_3$)	163	175	199	217
Reactor effluent pH	7,64	9,03	8,58	10,17

possible to give a conclusive reason for this difference in response. Probably the equilibrium established is a function of the solubility products of the precipitates making up the sludge. These solubility products are different by upto two orders of magnitude.

In the design of a lime treatment process the following information will be required,

(1) the relationship between pH and lime dosage,
(2) the pH for maximum alkalinity removal,
(3) the pH for maximum calcium removal,
(4) the pH for optimal magnesium removal, and
(5) the relationship between pH and mass of sludge generated.

Information on (1) to (4) can be read off directly from Figure 4.17 (a-d). Information on (5), i.e. sludge generated as a function of pH, can be calculated from the information presented in (1) to (4) (see foot notes to Table 4.11) and is plotted in Figure 4.18.

In order to check the validity of the application of the Modified Caldwell-Lawrence Diagram for predictive purposes, four basic relationships, i.e.

(1) Ca_T^{2+} versus pH,
(2) total alkalinity versus pH,
(3) lime dosage versus pH, and
(4) Mg_T^{2+} versus pH

were calculated. A Diagram (see Figure 4.19a) with temperature = 20°C; ionic strength = 0,015; pK_{CaCO_3} = 8,35; and $pK_{Mg(OH)_2}$ = 10,32 was used for this purpose. Calculational procedures as set out by Loewenthal and Marais (1976), when adding lime to a water, were used. The graphical solution on the Modified Caldwell-Lawrence Diagram is shown in Appendix 1.

Residual calcium vs pH

Experimentally determined and predicted relationships between residual total dissolved calcium, Ca_T^{2+}, and pH are illustrated in Figure 4.20(a). The two relationships are in fair agreement although the experimental Ca_T^{2+} values are in all cases slightly greater than the theoretical values over the pH range studied. The agreement is best in the pH range where calcium removal is optimal, i.e. 10,2 to 10,6, e.g. at pH 10,2,

$$Ca_T^{2+}(exp) - Ca_T^{2+}(pred) = 9 \text{ mg } \ell^{-1} (\text{as } CaCO_3)$$

The agreement deteriorates somewhat as the pH increases above 11,1 e.g. at pH 11,5,

$$Ca_T^{2+}(exp) - Ca_T^{2+}(pred) = 41 \text{ mg } \ell^{-1} (\text{as } CaCO_3)$$

The reasons for the discrepancies between the experimentally derived and predicted relationships are probably due to the following factors,

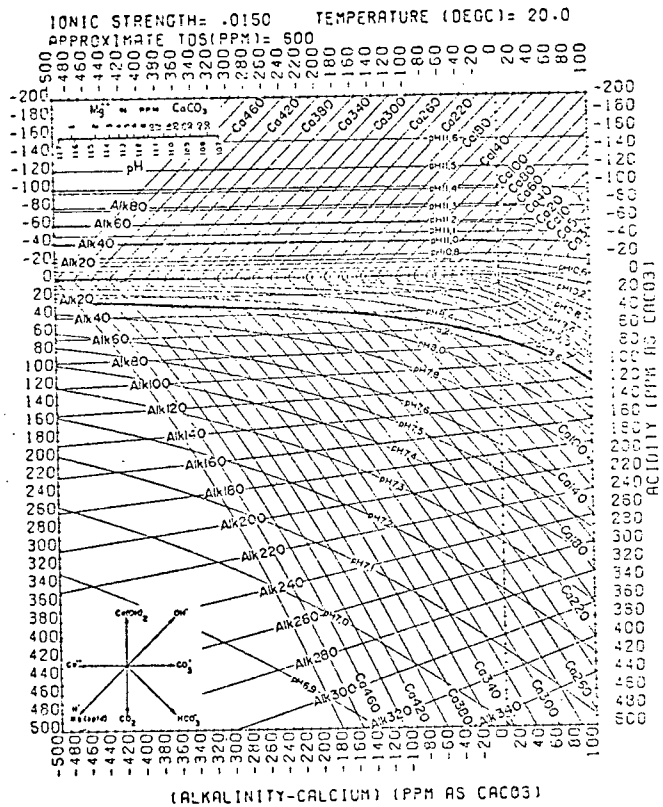


Figure 4.19(a). Modified Caldwell-Lawrence Diagram - neglecting ion pairing

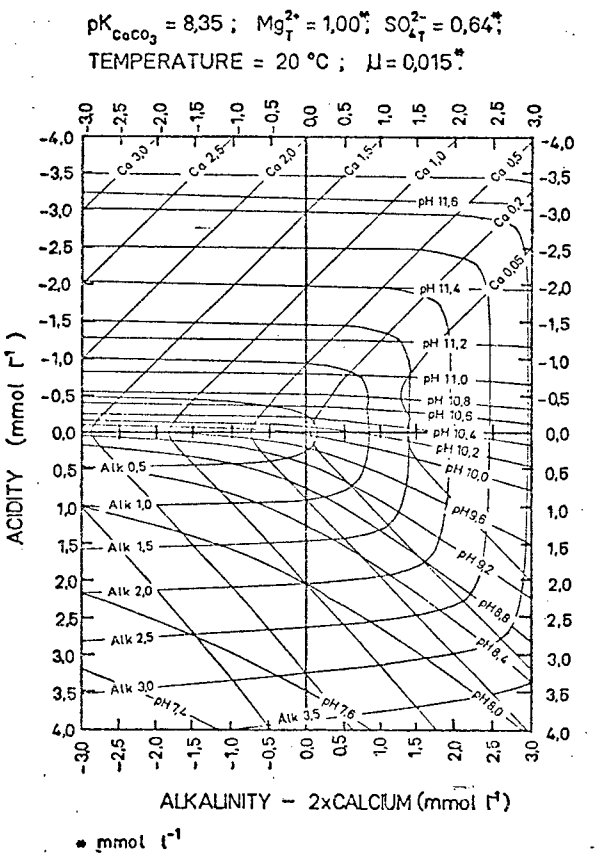


Figure 4.19(b). Modified Caldwell-Lawrence Diagram - incorporating ion pairing

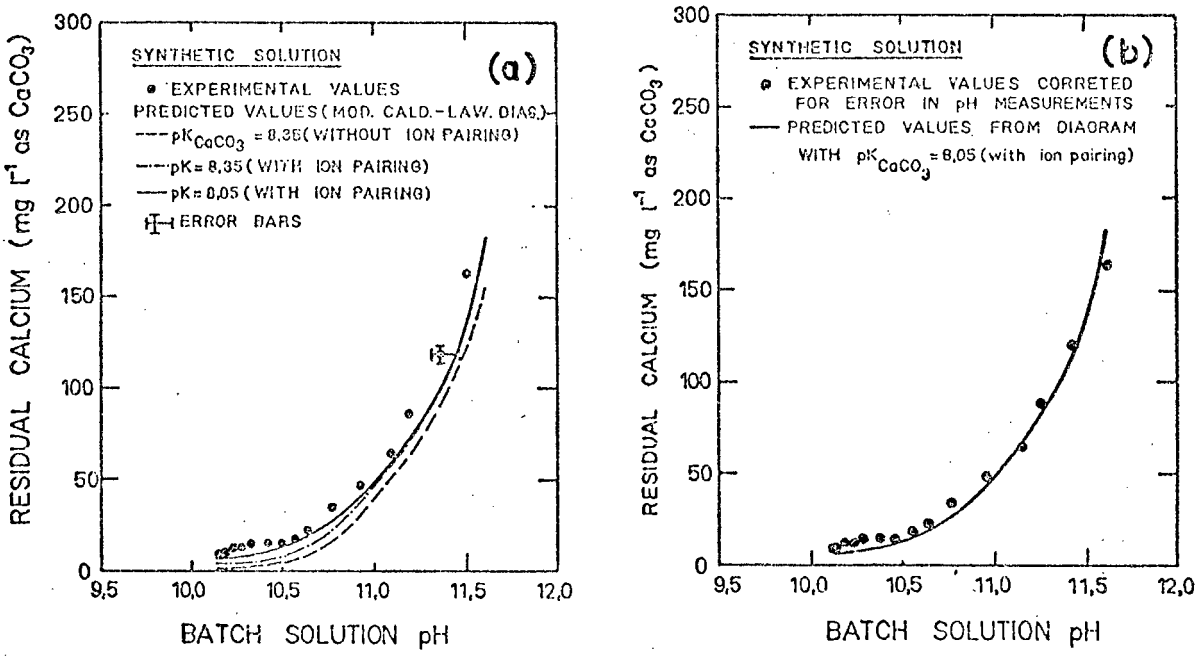


Figure 4.20(a-b). Experimental and predicted residual calcium concentration as a function of pH for a synthetic solution reacted in the presence of synthetic seed sludge (batch study)

(1) *Ion pairing* - The Modified Caldwell-Lawrence Diagram from which the predicted residual calcium values were obtained, neglects ion pairing. Ion pairs which are known to form in this type of system are $CaHCO_3^+$, $CaCO_3^o$, $CaOH^+$, $MgHCO_3^+$, $MgCO_3^o$ and $MgOH^+$. To correct for this effect Loewenthal (1977) has developed a new Diagram which incorporates ion pairing (see Figure 4.19(b)). This Diagram is less general than the old Diagram since it is specific for one magnesium and one sulphate value. However, this Diagram does give an improved fit between predicted and experimental values (see Figure 4.20a).

(2) *Effect of Magnesium* - The Diagram assumes $CaCO_3$ and $Mg(OH)_2$ to precipitate in the pure mineral forms of calcite and brucite. It does not consider precipitation of other forms of these two salts, e.g. aragonite and amorphous $Mg(OH)_2$, or compound salts such as

magnesian calcite. Benjamin, Loewenthal and Marais (1977) have reported that the presence of magnesium in solutions precipitating calcium carbonate alters the solubility of this calcium carbonate, i.e. for a Mg_T^{2+} :Ca_T^{2+} ratio of 20:1 (see Table 4.7, pH approximately 10,2), the apparent pK_{CaCO_3} value is 8,05 as compared to 8,35 for systems containing no magnesium. Using a Diagram with pK_{CaCO_3} = 8,05, the predicted values for Ca_T^{2+} are again closer to the experimental values than previously predicted (see Figure 4.20a).

(3) *Accuracy of pH measurements* - The pH meter used in these batch experiments was calibrated using two NBS standard buffers (Vogel, 1961), i.e. 0,025M Phosphate buffer (pH = 6,88 at 20°C) and 0,01M Borax buffer (pH = 9,22 at 20°C). Since the pH values for this specific experiment lie outside the range of the two abovementioned buffers, a range of secondary pH standard solutions was made up in the pH range 8,45 to 12,56, to test the accuracy of the pH measuring system calibrated with the Borax and Phosphate buffers. From the results in Table 4.9 it is clear that measured pH values may differ by -0,04 to -0,15 from the absolute pH values in the pH range 11,0 to 12,0. Therefore, the pH values determined in these effluent characterizing experiments should be considered to be too low, ranging from 0,05 at pH = 11 to 0,15 at pH = 12, as indicated by the error bars in Figure 4.20(a). The "true" pH (pH_T) may be estimated as follows :

$$pH_T = pH_M + 0,14\ (pH_M - 10,8) \quad \text{...for } pH_M \geq 10,8$$

$$pH_T = pH_M - 0,04 \quad \text{...for } pH_M < 10,8$$

Figure 4.20(b) illustrates the experimental and predicted residual calcium values as a function of pH, with experimentally measured pH values corrected according to the above two equalities for "true pH".

(4) *Thermodynamic Equilibrium* - The Modified Caldwell-Lawrence Diagram is based on the equilibrium chemistry of the calcium, magnesium, carbonic and water systems. In this experiment conditions, were chosen hopefully to achieve equilibrium rapidly, i.e. high seed mass of both $CaCO_3$ (7000 mg ℓ^{-1}) and $Mg(OH)_2$ (700 mg ℓ^{-1}), and fifteen minutes equilibration time. However, true thermodynamic equilibrium may only be

Table 4.8

"True" and measured pH values for secondary pH standards

pH_T, true pH values of 0,1M Glycine-NaOH mixtures (at 24°C)	pH pH_M Measured pH values	$pH_M - pH_T$	Temperature (°C)
8,45	8,94	+0,04	22,5
9,22	9,26	+0,04	22,5
10,32	10,35	+0,03	22,6
10,90	10,88	-0,02	22,7
11,14	11,10	-0,04	22,7
11,39	11,31	-0,08	22,8
11,92	11,77	-0,15	23,0
Absolute pH value of saturated $Ca(OH)_2$ solution at 22°C = 12,56	12,59	-0,03	22,2

established after hours or even days (see Chapter 6, Section 7). It is therefore expected that the experimental Ca_T^{2+} values will be slightly higher than the predicted values due to the system not having established true thermodynamic equilibrium (see Figure 4.20b)

Total alkalinity vs pH

Relationships between residual total alkalinity and pH for the synthetic sample are illustrated in Figure 4.21. As in the Ca_T^{2+} versus pH relationship, the correlation between the experimental and predicted values is excellent in the pH range 10,2 to 11,0, but less so at pH values higher than 11,0. As explained previously, these discrepancies may be partially attributed to inaccuracies in the pH measurements. Another contributary cause may be the adsorption of alkalinity contributing anions (OH^-, CO_3^{2-}) onto the calcium carbonate sludge, since it is reported in the literature (Black and Christman, 1961) that

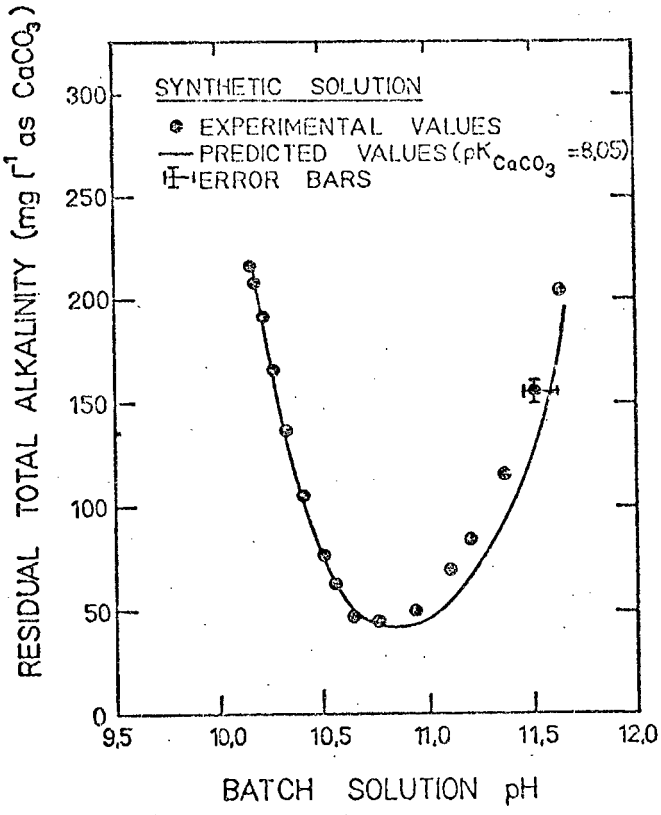


Figure 4.21. Experimental and predicted Alkalinity concentration as a function of pH for a synthetic solution (batch study)

$CaCO_3$ sludge particles are usually negatively charged.

Lime dosage vs pH

Figure 4.22 illustrates experimentally determined and predicted relationships between lime dosage and pH. The correlation between the experimental and predicted values is excellent for pH values in the range 10,2 to 10,5, but appears to deteriorate steadily with increasing pH above 10,5. It is interesting to note that the ratio of the experimentally determined lime demand to the predicted lime demand is approximately constant at 1,11 (see Table 4.9). This suggest that the experimentally determined lime dosage may be fairly accurately calculated using 1,11 as a correction factor, i.e.

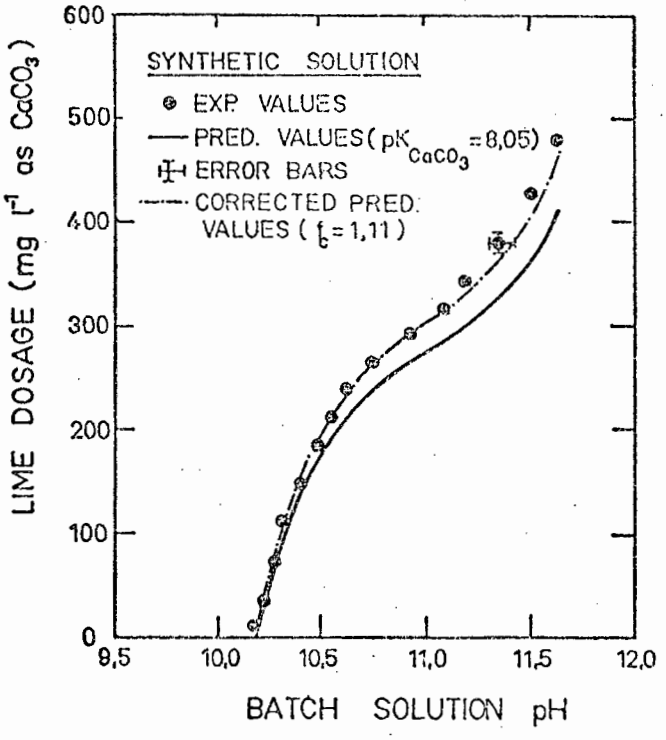


Figure 4.22. Relationship between experimental and predicted lime dosage and pH for a synthetic solution (batch test)

Table 4.9

Lime demand of a synthetic solution

Solution pH	10,50	10,56	10,64	10,76	10,93	11,10	11,20	11,26
Exp. Lime Demand* (LD_E)	187	220	240	266	293	319	343	381
Pred. Lime Demand* (LD_P)	175	194	217	241	266	288	301	326
LD_E/LD_P	1,07	1,09	1,11	1,10	1,10	1,11	1,14	1,17

*mg l^{-1} as $CaCO_3$.

$$LD_E \simeq 1,11 x LD_P \quad \ldots\ (4.20)$$

where LD_E = experimentally determined lime demand (mg ℓ^{-1} as $CaCO_3$)

LD_P = predicted lime demand (mg ℓ^{-1} as $CaCO_3$)

The discrepancy between experimental and predicted lime dosages is probably due to the following factors,

(1) *Incomplete lime dissolution* - will result in experimental pH values lower than the predicted values, as observed in Figure 4.22. Incomplete lime dissolution could result due to $CaCO_3$ precipitation on dissolving $Ca(OH)_2$ particles, hindering further dissolution (Jenkins and Lee, 1976).

(2) *Error in the pH measurement* - As previously explained.

Residual magnesium vs pH

Experimentally determined and predicted relationships between residual total dissolved magnesium, Mg_T^{2+}, and pH are illustrated in Figure 4.23. Predicted Mg_T^{2+} values, based on $pK_{Mg(OH)_2}$ values ranging between 10,0 and 11,7, are shown. The experimental Mg_T^{2+} versus pH relationship is predicted fairly accurately by $pK_{Mg(OH)_2} = 10,7$.

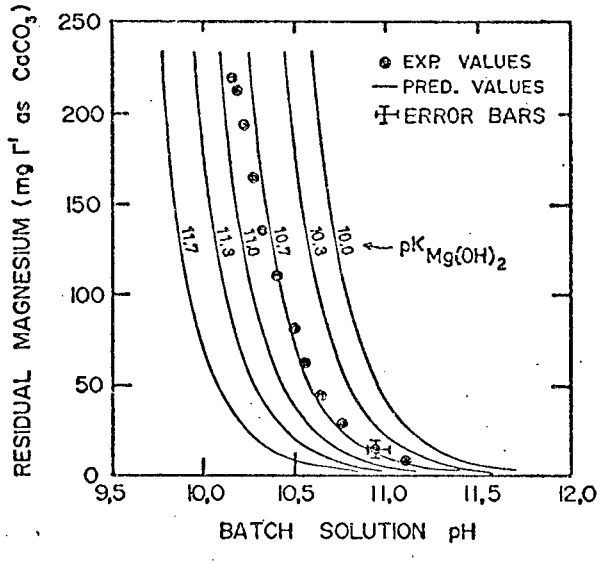


Figure 4.23. Experimental and predicted residual magnesium concentration as a function of pH for a synthetic solution (batch test)

In the literature there appears to be no agreement on the value for the magnesium hydroxide solubility product value. Values ranging from 9,5 to 11,9 have been reported (see Chapter 2, Section 2.3). The $pK_{Mg(OH)_2}$ value found in this study is in good agreement with the value reported by Travers and Nouvel (1929), i.e. 10,67 at 20°C. The reason for the divergence in literature reported experimentally determined $pK_{Mg(OH)_2}$ values is thought to be the existence of two forms of $Mg(OH)_2$, a labile amorphous precipitate with a high solubility (low pK value) and a stable crystalline precipitate with a lower solubility (higher pK value)(Gjaldbaek, 1925).

Sludge generated vs pH

Experimentally derived and theoretically calculated masses of sludge ($CaCO_3$ + $Mg(OH)_2$) generated as a function of pH are shown in Figure 4.24. Theoretically calculated masses of sludge generated, were obtained from a

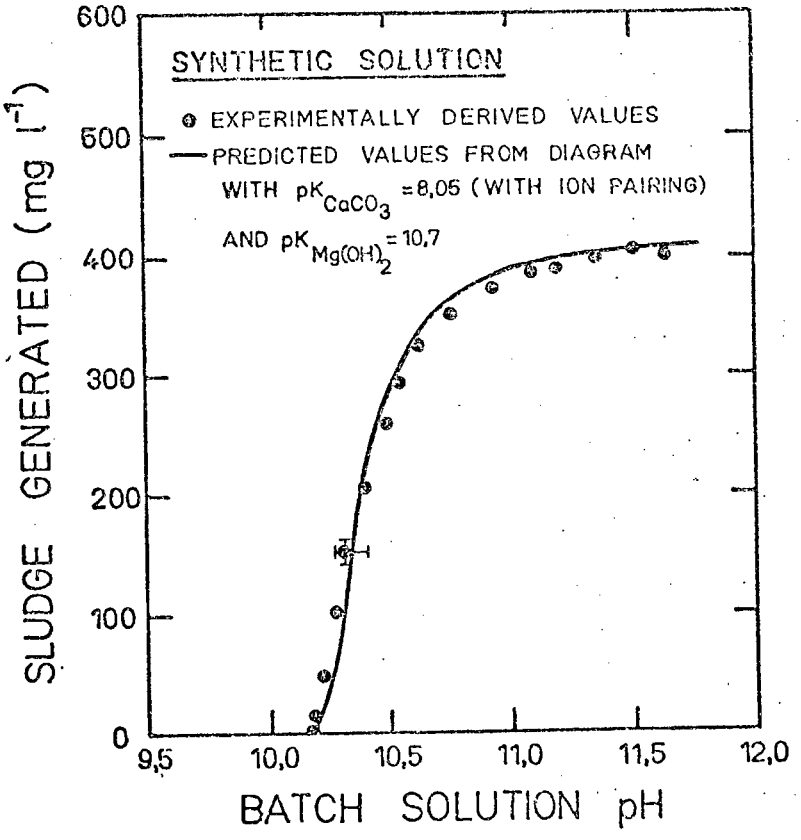


Figure 4.24. Experimentally derived and theoretically calculated masses of sludge generated as a function of pH for a synthetic solution (batch test)

Modified Caldwell-Lawrence Diagram (incorporating ion-pairing) with pK_{CaCO_3} = 8,05 and $pK_{Mg(OH)_2}$ = 10,7. The correlation between the experimental and theoretical values is excellent, indicating the validity of the Diagram for predicting masses of sludge generated as a function of pH for synthetic solutions.

From the above results it may be concluded that the basic relationships which characterize a lime-treated solution, i.e. the relationship between pH and Ca_T^{2+}, Alkalinity and lime dosage may be adequately predicted using a Modified Caldwell-Lawrence Diagram in which ion pairing and the effect of Mg^{2+} on the solubility of calcium carbonate is considered. The relationship between residual magnesium and pH is adequately predicted by using a monograph based on $pK_{Mg(OH)_2}$ = 10,7 (see Appendix 1). Sludge generated as a function of pH can as a consequence also be predicted adequately.

5.3 Lime-Treated Secondary Effluent

Quality changes affected by the addition of lime to secondary effluent are listed in Table 4.10. Experimentally determined relationships between pH and lime dosage, total alkalinity and residual total dissolved calcium and magnesium are graphically illustrated in Figure 4.25(a-d). These plots characterize the response of this particular secondary effluent to lime treatment. The masses of $CaCO_3$, lime insolubles, $Ca_3(PO_4)_2$ and $Mg(OH)_2$ which form at the various pH values were calculated from the data in Table 4.10 and are listed in Table 4.11. Using these calculated masses an estimate can be made of the total mass of sludge generated at various pH values, excluding contributions due to organic matter (which are

Table 4.10

Typical experimental results for secondary effluent lime treatment (batch test)

LIME DOSAGE	REACTOR EFFLUENT pH	FILTERED REACTOR EFFLUENT pH	TOTAL ALKALINITY	TOTAL DISSOLVED CALCIUM	TOTAL DISSOLVED MAGNESIUM	ORTHO-PHOSPHATE	COD	AMMONIA
$mg\ \ell^{-1}$ (as $CaCO_3$)	-	-	$mg\ \ell^{-1}$ (as $CaCO_3$)	$mg\ \ell^{-1}$ (as $CaCO_3$)	$mg\ \ell^{-1}$ (as $CaCO_3$)	$mg\ \ell^{-1}$ (as PO_4-P)	$mg\ \ell^{-1}$ (as O)	$mg\ \ell^{-1}$ (as NH_3-N)
Effluent only	7,64	7,82	163	103	91	6,2	25	5,1
Effluent & sludge	9,03	9,00	175	95	99	1,9	24	4,6
21	9,33	9,28	181	98	103	1,3	20	4,3
52	9,61	9,56	190	108	103	0,8	19	4,5
93	9,91	9,85	201	125	99	0,4	19	4,5
144	10,22	10,10	187	118	87	0,2	22	4,1
204	10,51	10,35	144	105	58	0,1	21	4,1
274	10,81	10,67	112	110	25	0,1	21	4,0
344	11,15	11,03	126	140	4	0,1	25	4,0
414	11,40	11,32	168	188	4	0,1	22	4,1
482	11,58	11,47	221	243	4	0,1	18	4,4
550	11,66	11,59	255	269	4	0,1	16	4,3

Reaction temperature = 20-22°C; %Active Lime = 78,6% (as $Ca(OH)_2$)

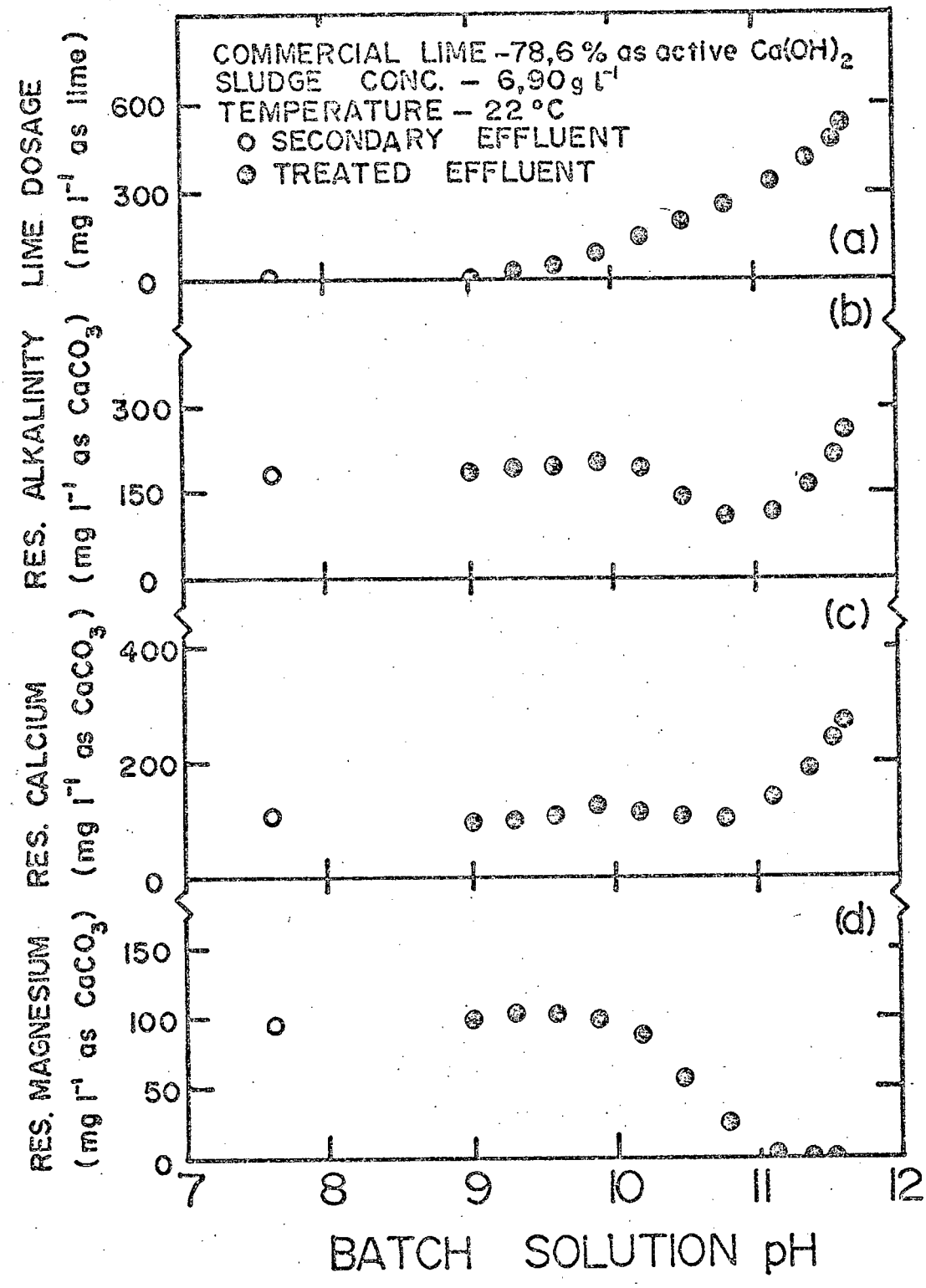


Figure 4.25(a-d). Plots indicating the response of secondary effluent to lime treatment in the presence of sludge (batch test)

Table 4.11

Various components contributing to the inorganic mass precipitated during lime treatment of secondary effluent in the presence of inoculated seed sludge (batch test)

Effluent pH	$CaCO_3$ *	Non-Active** Lime Fraction	$Ca_3(PO_4)_2$***	$Mg(OH)_2$ †	Inorganic†† Sludge generated
9,33	15	4	25	0	44
9,61	33	11	27	0	71
9,91	55	19	29	2	105
10,22	118	30	30	9	187
10,51	193	43	31	26	293
10,81	260	58	31	45	394
11,15	305	73	31	57	466
11,40	330	88	31	57	506
11,58	350	103	31	57	541
11,66	375	113	31	57	576

All parameters reported as mg ℓ^{-1}, except the pH.

*$CaCO_3 = 2,5 \times (Ca_{in} + Ca_{ACT.LIME} - Ca_{out} - Ca_{Ca_3(PO_4)_2})$

**Non Active Lime Fraction (N.A.L.F.) = 0,214 *lime dosage

***$Ca_3(PO_4)_2 = 5,00 \times \{(PO_4\text{-}P)_{in} - (PO_4\text{-}P)_{out}\}$

†$Mg(OH)_2 = 2,40 \times (Mg_{in} - Mg_{out})$

††Inorganic Sludge Generated = $CaCO_3$ + N.A.L.F. + $Ca_3(PO_4)_2$ + $Mg(OH)_2$

relatively small in the case of secondary effluent).

The effect of sludge addition only to secondary effluent, i.e. in the absence of any added lime, is illustrated in Table 4.7. The major effects were: raising the pH of the reaction solution from 7,64 to 9,03 and a significant reduction (69 percent) in the ortho-phos-

phate content. The increase in pH is due to the high pH of the sludge (pH = 9,63). The phosphate removal is due to the increase in pH with subsequent tricalcium phosphate precipitation and possibly some ortho-phosphate adsorption on the $CaCO_3$ particles in the sludge (see Chapter 2, Section 4.1). Other smaller effects of sludge addition to secondary effluent were : small changes in the concentrations of dissolved total alkalinity, calcium and magnesium. These minor changes were due to $Ca_3(PO_4)_2$ and $CaCO_3$ precipitation and $Mg(OH)_2$ dissolution.

The characterization curves given in Figure 4.24 and the data listed in Tables 4.10 and 4.11 may be usefully applied for design purposes to select a lime dosage(s) to achieve a specific objective(s) for the treatment of an effluent. For example, for this specific secondary effluent,

(1) Optimal total alkalinity removal takes place in the pH range 10,4 to 10,5.

(2) Optimal ortho-phosphate removal takes place in the pH range 10,0 to 10,5.

(3) The residual total dissolved calcium concentration remains practically unchanged in the pH range 9,0 to 11,0, but maintains a high level of approximately 100 mg ℓ^{-1} (as $CaCO_3$).

(4) Significant magnesium removal takes place over the pH range 10,2 to 11,2.

(5) Marginally improved removal of dissolved COD takes place at pH values greater than 10,0.

From Table 4.11 it is clear that the mass of sludge generated increases with increasing pH. Therefore, to ensure minimum sludge generation, the minimum pH and hence lime addition to achieve a specific objective should be adhered to.

It would be advantageous if the characterizing relationships could be predicted instead of being determined experimentally. If such a prediction is reliable it would be unnecessary to conduct an experimental investigation, or, isolated check values only need to be done. At present the most simple and rapid predictive tool available for doing

this is the Modified Caldwell-Lawrence Diagram.

Residual calcium versus pH

Experimentally determined and predicted relationships between residual total dissolved calcium, Ca_T^{2+}, and pH are illustrated in Figure 4.26. The predicted relationship was obtained from a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 8,35. The correlation between predicted and experimental Ca_T^{2+} values is poor, e.g. at pH 9,0,

$$Ca_T^{2+} \text{ (exp.)} - Ca_T^{2+}\text{(pred.)} = 80 \text{ mg } \ell^{-1} \text{ (as } CaCO_3)$$

and at pH 10,0,

$$Ca_T^{2+}\text{(exp.)} - Ca_T^{2+}\text{(pred.)} = 115 \text{ mg } \ell^{-1} \text{ (as } CaCO_3)$$

and at pH 11,0,

$$Ca_T^{2+}\text{(exp.)} - Ca_T^{2+}\text{(pred.)} = 72 \text{ mg } \ell^{-1} \text{ (as } CaCO_3)$$

Application of the Diagram with pK_{CaCO_3} = 8,3 presumes that pure system equilibrium conditions hold for such a system. This is obviously not the case for lime-treated secondary effluent. This system is considerably more complex than the pure system, i.e. it contains ortho-phosphates, organic phosphates, other organic matter and magnesium, all of which may affect the rate of precipitation and the final equilibrium state of the calcium carbonate system. A detailed review of the effects these compounds have on the $CaCO_3$ system is given in Chapter 2, Section 4. From this literature review it was concluded that all these compounds, but specifically phosphates have a very pronounced inhibiting effect on $CaCO_3$ precipitation and give rise to increased $CaCO_3$ solubility. These effects possibly can be incorporated in the Diagram by increasing the calcium solubility product.

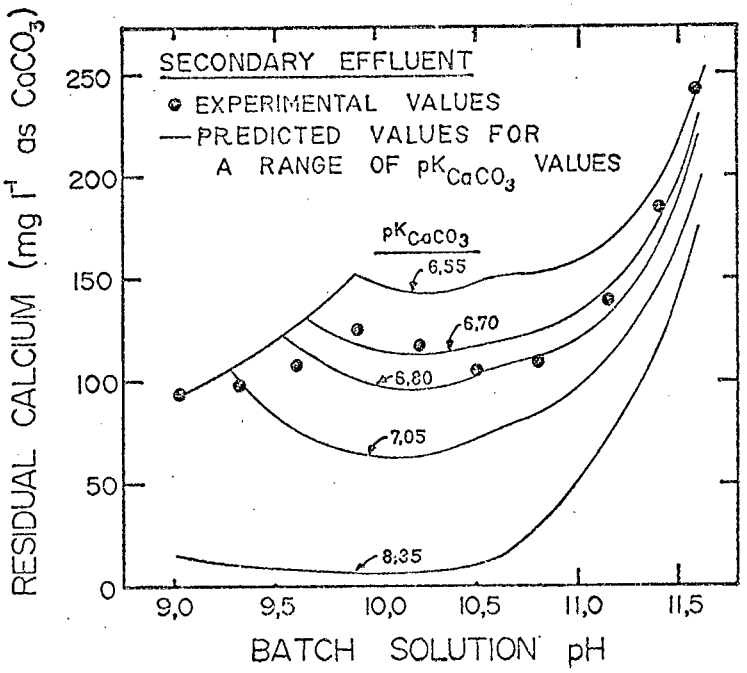


Figure 4.26. Experimental and predicted residual calcium concentration as a function of pH for lime-treated secondary effluent reacted in the presence of seed sludge (batch tests)

Predicted relationships between Ca_T^{2+} and pH derived from Diagrams with apparent pK_{CaCO_3} values ranging from 8,35 to 6,55, are illustrated in Figure 4.26. It is clear that the experimental Ca_T^{2+} values for the whole pH range studied cannot be accurately predicted using only one pK value, although reasonable results were arrived at by using a Diagram with $pK_{CaCO_3} = 6,7$, e.g. at pH = 9,0,

$$Ca_T^{2+}(\text{exp.}) - Ca_T^{2+}(\text{pred.}) = 0 \text{ mg } \ell^{-1} \text{ (as } CaCO_3)$$

and at pH = 10,0,

$$Ca_T^{2+}(\text{exp.}) - Ca_T^{2+}(\text{pred.}) = 5 \text{ mg } \ell^{-1} \text{ (as } CaCO_3)$$

and at pH = 11,0,

$$Ca_T^{2+}(exp.) - Ca_T^{2+}(pred.) = 10 \text{ mg } \ell^{-1} (as\ CaCO_3)$$

The above results are by far superior to those predicted using a Diagram with $pK_{CaCO_3} = 8,35$ (see Figure 4.26) and should serve adequately for all practical predictive purposes. The reason for the slight deviations (0-25 mg ℓ^{-1} as $CaCO_3$) in the predicted values from the experimental values is attributed to the simplicity of the model, i.e. the model contains only one constant ($pK_{CaCO_3} = 6,70$) as compared to the complexity of the system being modelled.

Residual total alkalinity versus pH

Experimentally determined and predicted relationships between residual total alkalinity and pH are illustrated in Figure 4.27. Predicted relationships from Diagrams with $pK_{CaCO_3} = 8,35$ and 6,70 are shown. Predictions from the Diagram with pK = 6,70 are far superior to those from the Diagram with pK = 8,35. The correlation between predicted values (pK = 6,70) and experimental values is reasonable - on the average within 10 percent and hence sufficiently accurate for practical predictive purposes.

Lime dosage vs pH relationship

Figure 4.28 illustrates the experimentally determined and predicted relationships between lime dosage and pH. The correlation between the experimental and the predicted relationships is fair at the lower pH values but deteriorates with increasing pH. There are a number of reasons why one would expect the experimental lime demand to be higher than the lime demand predicted from a Diagram, i.e.

(1) *Phosphate lime demand* - The predicted lime demand is based on the assumption that the effluent-lime system consists of only the $CaCO_3$ and $Mg(OH)_2$ sub-systems. However, the ortho-phosphate present in secondary effluent also exerts a lime demand, i.e.

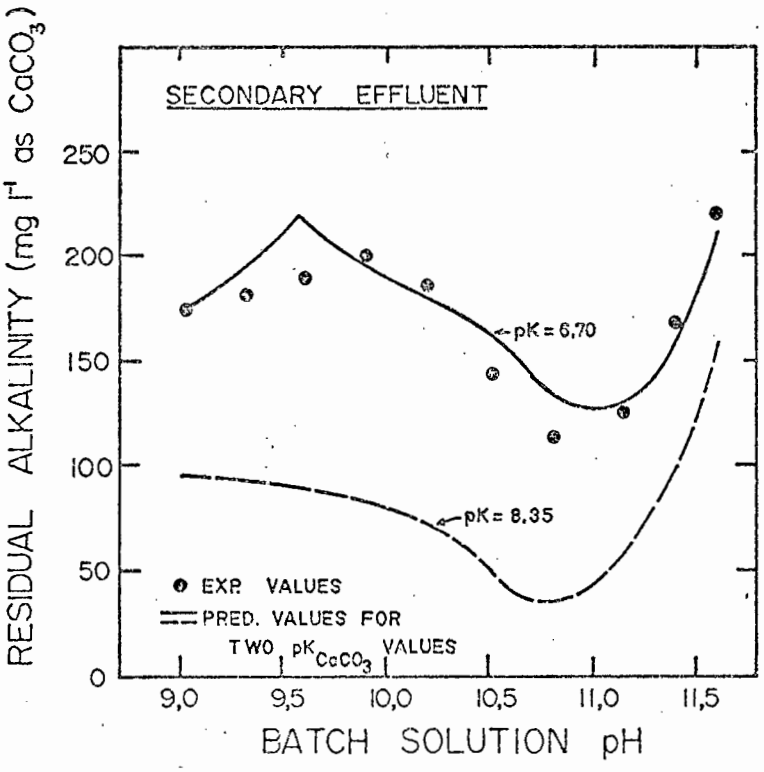


Figure 4.27. Experimental and predicted residual Alkalinity concentration as a function of pH for lime-treated secondary effluent (batch test)

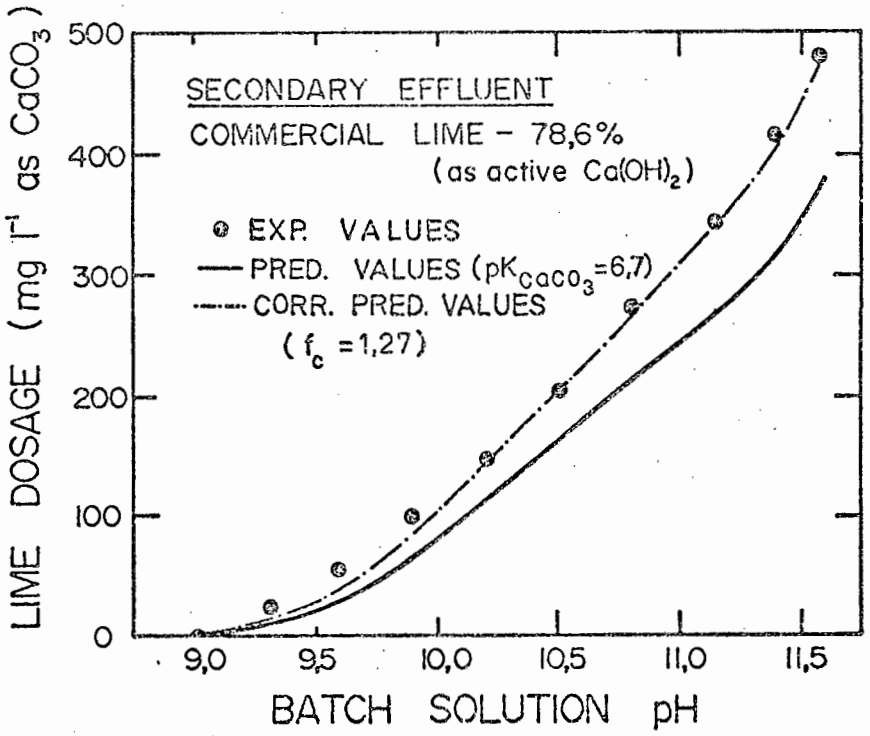


Figure 4.28. Experimental and predicted lime dosages as a function of pH for lime-treated secondary effluent. (batch test)

$$2H_2PO_4^- + 3\ Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + 2OH^- + 4H_2O \quad .... \quad (4.21)$$

and hence,

1 mg ℓ^{-1} ortho-phosphate(as P) $\equiv$ 4,84 mg ℓ^{-1} lime(as $CaCO_3$)

In the case of this specific secondary effluent, which has an ortho-phosphate concentration of 1,9 mg ℓ^{-1}(as P) after sludge addition, an extra lime demand of 9,2 mg ℓ^{-1}(as $CaCO_3$) can be expected for the complete precipitation of all the ortho-phosphate as tri-calcium phosphate, at pH values higher than 10,5.

(2) *Ammonia lime demand* - The secondary effluent contains ammonia in the NH_4^+ form. On lime treatment this ionic species will be converted to the NH_4OH form (see Chapter 7, Figure 7.17) and hence exert a lime demand, i.e.

$$NH_4^+ + \tfrac{1}{2}Ca(OH)_2 \longrightarrow NH_4OH + \tfrac{1}{2}Ca^{2+} \quad .... \quad (4.22)$$

and hence

1 mg ℓ^{-1} ammonia(as N) $\equiv$ 2,64 mg ℓ^{-1} lime(as $Ca(OH)_2$)

This specific secondary effluent has an ammonia concentration of 4,6 mg ℓ^{-1}(as N) after sludge addition and hence an extra lime demand of 12 mg ℓ^{-1} lime(as $CaCO_3$) will be required for the complete conversion of the ammonia ions to ammonium hydroxide which takes place at pH values greater than approximately 11,0.

(3) *Lime demand of other misceallaneous components* - In addition to the lime demand of the ortho-phosphate and ammonium ions which can be quantified, secondary effluent-sludge systems contain other components which may also excert a lime demand which

cannot at this stage be quantified, i.e.

(a) *Organic matter* - It has been reported that waste water organic matter exerts a lime demand (Folkman and Wachs, 1973). However, the lime demand of organic matter will depend on the specific nature of the organic compounds and the experimental conditions, such as pH. A general correlation between say COD and lime demand is therefore not expected.

(b) *Sludge* - may exert a lime demand i.e. the material which makes up the sludge is not necessarily inert, but may react with lime. It is for instance conceivable that calcium and hydroxide ions may adsorb onto the sludge, specifically onto $CaCO_3$ particles. Sludge used in this experiment was rinsed with secondary effluent in an effort to remove water-phase contaminating species from the original sludge and also to bring the pH of the sludge down to that of secondary effluent. After copious rinsing the pH of the sludge decreased from 11,2 to 9,6. It may therefore be expected that raising the pH of this low pH sludge back to 11,2 or higher will again require lime.

It was attempted to determine the lime demand of sludge as follows : Sludge was drawn from the Stander Plant primary clarifier; The sludge was rinsed with copious quantities of secondary effluent as described in Section 5.1 reducing the sludge pH from 11,2 to 9,6; It was then rinsed with copious quantities of distilled water. The relationship between lime dosage and pH for the sludge-distilled water mixture was then determined, as illustrated in Figure 4.29. The sludge-distilled water system was chosen in order to minimize lime demand due to water phase components such as Ca^{2+}, HCO_3^-, Mg^{2+}, $H_2PO_4^-$, etc, normally present in effluent. It is clear from Figure 4.29 that the experimentally determined lime demand far exceeds the low predicted lime demand of the distilled water in equilibrium with the sludge.

It is possible that the sludge lime demand determined in this study is excessively high, since sludge was inoculated into a batch solution at a pH value considerably lower than the pH values to which the effluent is subsequently treated with lime. A practical solution to the prediction of an effluent-sludge system's lime demand is set out below. From this study it is concluded that lime demand of sludge is primarily a function of the pH to which one wishes to raise the sludge.

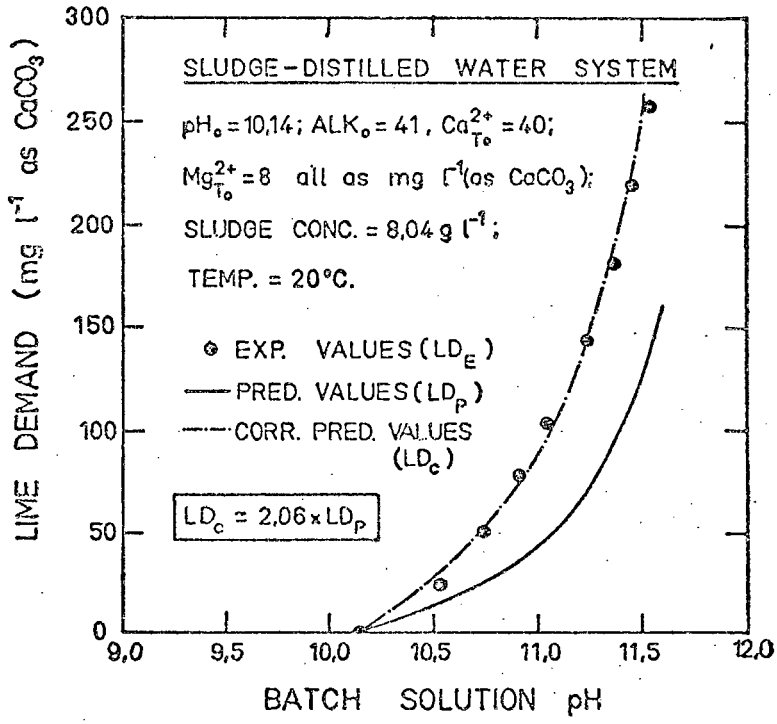


Figure 4.29. Experimental and predicted lime demand as a function of pH for a sludge-distilled water system (batch test)

(4) *Incomplete lime dissolution* - Another explanation for the discrepancy between predicted and experimentally determined lime demand may be incomplete lime dissolution. Merrill (1974) came to this conclusion when he measured discrepancies of 10 to 25 percent between predicted and experimentally determined lime dosages for lime-treated raw sewage. However, since in the present investigation considerably longer dissolution times were allowed, i.e. 15 minutes after each lime addition and approximately 4 hours for the whole test, this effect is probably minimal. However, it is conceivable that due to the presence of heterogeneous substances in secondary effluent, precipitation of $CaCO_3$ may take place at the dissolving $Ca(OH)_2$ surface, partially or completely blocking any subsequent lime dissolution.

Table 4.12 lists predicted and experimentally determined lime demands. It is interesting to note, as in the case of the pure system, that there is an approximately constant relationship between the experimentally determined lime dosage (LD_E) and predicted lime dosage (LD_P), i.e.

$$LD_E \simeq 1{,}27 \times LD_P \quad \ldots \quad (4.22)$$

It is therefore possible to make a fairly accurate prediction of the actual lime dosages which will be required in practice. The percentage of "unaccounted" lime demand in the case of secondary effluent, i.e. 21 percent, is considerably higher than in the case of the pure system, i.e. 10 percent. The difference can only be due to factors specific to the secondary effluent, i.e. lime demand of the phosphates, ammonia, organic matter, sludge and the inhibition of lime dissolution by the heterogeneous components.

Table 4.12

Experimentally determined and predicted lime demand of secondary effluent

Solution pH	10,4	10,6	10,8	7,0	11,2	11,4
Exp. Lime Demand* (LD_E)	180	222	273	310	388	418
Pred. Lime Demand* (LD_P)	145	181	214	248	279	318
LD_E/LD_P	1,24	1,23	1,28	1,25	1,28	1,31

*mg ℓ^{-1} (as $CaCO_3$)

Residual magnesium versus pH

Experimentally determined and predicted relationships between residual total dissolved magnesium and pH are illustrated in Figure 4.30. Based on the assumption that the residual magnesium concentration, Mg_T^{2+}, is controlled by magnesium hydroxide precipitation only, it should be possible to calculate the relationship between Mg_T^{2+} and pH from the equilibrium model,

$$K_{Mg(OH)_2} = (Mg^{2+})(OH^-)^2 \quad \ldots\ldots \quad (4.23)$$

This model was demonstrated to give accurate predictions for the Mg_T^{2+} versus pH relationship for the pure system (see Section 5.2). However, it is obvious from Figure 4.30 that the relationship between Mg_T^{2+} and pH is not well modelled by one $K_{Mg(OH)_2}$ value. The $K_{Mg(OH)_2}$ value appears to be a function of pH, at pH values less than 10,5, as is substantiated by a plot of $pK_{Mg(OH)_2}$ versus pH (see Figure 4.31), i.e.

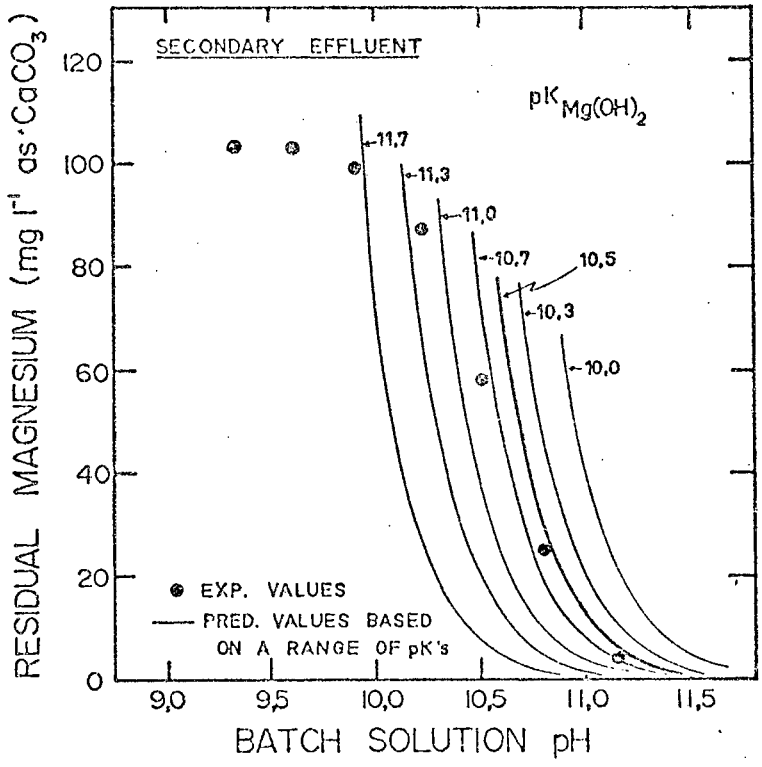


Figure 4.30. Experimental and predicted residual magnesium concentration as a function of pH for lime-treated secondary effluent reacted in the presence of seed sludge (batch tests)

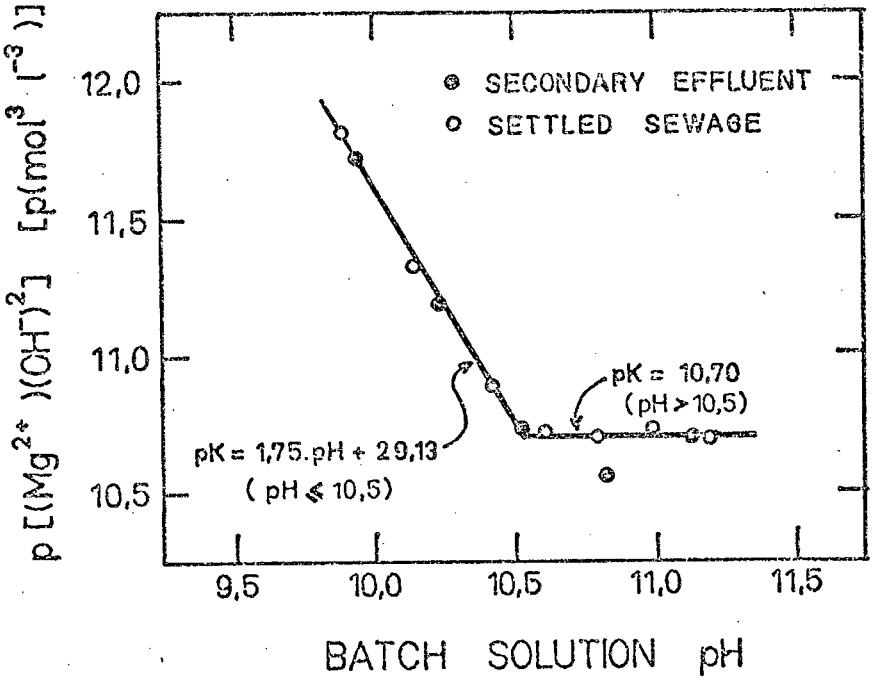


Figure 4.31. $Mg(OH)_2$ activity product constants as a function of pH for Pretoria Sewage Works lime-treated secondary effluent and settled sewage reacted in the presence of seed sludge (batch tests)

$$pK_{Mg(OH)_2} = -1,75pH + 29,13 \quad .... \ 9,8<pH<10,5 \ ... \ .... \quad (4.24)$$

but is constant at pH values greater than 10,5, i.e.

$$pK_{Mg(OH)_2} = 10,70 \quad .... \ 10,5<pH<11,3 \ .... \quad (4.25)$$

Two possible explanations for these observations are,

(1) *The existence of two forms of* $Mg(OH)_2$ - Gjaldbaek (1925) suggested that two forms of $Mg(OH)_2$ precipitate from solution (see Chapter 2, Section 2.3), i.e. a stable crystalline form having a low solubility (high pK value) which only forms under conditions of slight supersaturation (low pH values); and an amorphous form having a higher solubility (lower pK value) which forms under conditions of high supersaturation (higher pH values). Between the two extremes it is possible that co-precipitation of these two forms takes place in changing proportion as the pH is raised, resulting in the variation of pK with pH.

(2) *Magnesium removal by mechanisms other than* $Mg(OH)_2$ *precipitation* - It is known that magnesium may be removed from solutions by a number of mechanisms other than $Mg(OH)_2$ precipitation, i.e. as magnesian-calcite, magnesium silicate and magnesium adsorption onto $CaCO_3$ particles (see Chapter 2, Section 4.2). When these mechanisms are operative, Eq. (4.23) cannot be expected to hold and hence describe the precipitation states. The measured $(Mg^{2+})(OH^-)^2$ values then are not expected to be constant. However, at the higher pH values the magnesium hydroxide mechanism for magnesium removal dominates, due to the high potential for $Mg(OH)_2$ precipitation as a result of the high OH^- concentration. Hence, Eq. (4.23) should hold and $(Mg^{2+})(OH^-)^2$ values can be expected to remain constant, which is in fact the case at pH values higher than about 10,5.

Substantive proof for either of these two hypotheses is not available, due to the difficulty in identifying magnesium precipitates in a sludge which consists predominantly of $CaCO_3$. However, for practical purposes the constant $pK_{Mg(OH)_2}$ value given by Eq. (4.25)

will suffice, since lime treatment in water reclamation is usually operative at pH values well above pH 10,5, i.e. 11,0 - 11,6.

Merrill (1974) reported experimentally determined $pK_{Mg(OH)_2}$ values for lime-treated raw sewage which are apparently linearly related to pH, i.e.

$$pK_{Mg(OH)_2} = 25,537 - 1,382\ pH \quad .... \ 10,5<pH<11,5 \quad .... \ (4.26)$$

Merrill (1974) speculated that the variation in $pK_{Mg(OH)_2}$ with pH is due to the existence of unidentified ion group species, e.g. $Mg(OH)_2^o$ and $Mg(OH)_3^-$, but no supporting evidence was presented. From the description of his experimental procedure (see Chapter 2, Section 5.2), no sludge was added to the reaction vessel and hence the opportunity for establishing $Mg(OH)_2$ equilibrium was greatly reduced. The pK variation with pH is therefore more likely due to incomplete precipitation, since magnesium hydroxide precipitation in the absence of high seed $Mg(OH)_2$ concentrations is a slow process (Liu and Nancollas, 1973)(also see Section 3.2).

Sludge generated vs pH

Using a Modified Caldwell-Lawrence Diagram with $pK_{CaCO_3} = 6,70$ and $pK_{Mg(OH)_2} = 10,7$ it is possible to estimate the mass of inorganic sludge generated as a function of pH. Figure 4.32 illustrates the experimentally derived and theoretically predicted masses of sludge generated as a function of pH. The correspondence between the experimental and predicted values is generally good, with exception in the low pH range (9,2 - 9,8) where the predicted masses of sludge are somewhat lower (max. 30 mg ℓ^{-1}) than those determined experimentally. This deviation was expected as is evident from Figure 4.26.

It is concluded that the five basic relationships characterizing lime-treated secondary effluent, i.e. the relationships between pH and residual calcium, residual total alkalinity, lime dosage, residual

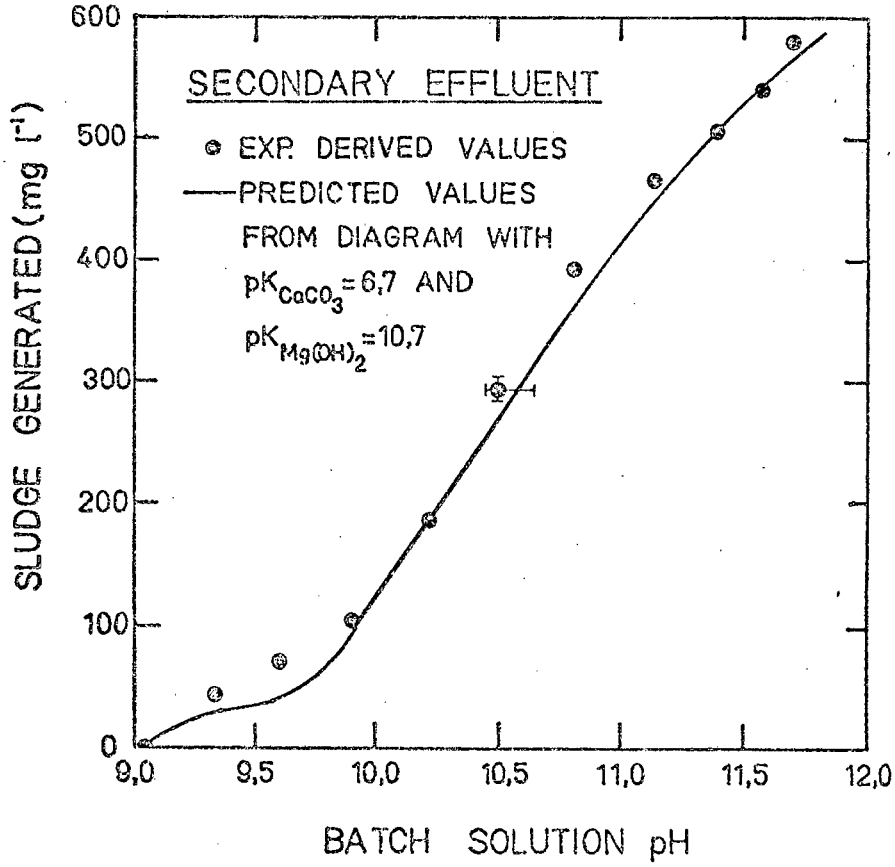


Figure 4.32. Experimentally derived and theoretically predicted masses of sludge generated as a function of pH for lime-treated secondary effluent reacted in the presence of seed sludge (batch test)

magnesium and sludge generated may be adequately predicted for practical purposes using a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 6,7 and $pK_{Mg(OH)_2}$ = 10,70 provided sufficient sludge is present to drive the reactions to completion within practical reaction times, i.e. 5-10 minutes.

5.4 Lime-Treated Settled Sewage

In the previous section lime-treated secondary effluent was characterized. Models were developed for predicting the characterizing relationships between pH and the major system parameters. In this section lime-treated settled sewage is characterized. The validity of the predictive model developed for secondary effluent is tested for

this stronger sewage effluent.

Typical experimental results are listed in Table 4.13. The experimentally determined relationships between pH and lime dosage, total alkalinity, residual total dissolved calcium and magnesium, are illustrated in Figure 4.33 (a-d). These plots characterize the response of this particular settled sewage to lime treatment. From the data in Table 4.13 the theoretical quantities $CaCO_3$, lime insolubles, $Ca_3(PO_4)_2$ and $Mg(OH)_2$ which formed at various pH values were calculated and are listed in Table 4.14. The sum of these constituents gives an estimate of the total mass of the inorganic fraction of the sludge. The organic fraction could not be predicted with any accuracy since the exact relationship between COD removed and mass of organic matter removed was not known. However, an approximation can be made by assuming the following relationship between volatile solids (VS) and COD (Marais, 1978), i.e.

$$VS = \frac{COD}{1,42} = 0,7\ COD \quad \ldots\ (4.27)$$

Comparing the chemical composition of the settled sewage studied in this experiment with that of the secondary effluent discussed in the previous section (see Table 4.15) the only major differences between the two effluents are the higher dissolved and suspended organic matter in the settled sewage. The inorganic components, with the exception of the ammonia, all lie within 0-20 percent of each other. Of specific interest from the point of view of calcium carbonate precipitation, is that the ortho- and organic phosphate concentrations are very similar in these two effluents. Comparing the characterization curves for lime-treated settled sewage (Figure 4.33 (a-d)) with those for lime-treated secondary effluent (Figure 4.25 (a-d)) it is noted that,

(1) Lime demand to achieve pH 11,0,

Secondary effluent - 300 mg ℓ^{-1} (as lime)
Settled sewage - 325 mg ℓ^{-1} (as lime)

(2) pH range for maximum alkalinity removal,

Secondary effluent - 10,8 - 11,0
Settled sewage - 10,8 - 11,0.

Table 4.13

Typical experimental results for settled sewage lime treatment

LIME DOSAGE	REACTOR EFFLUENT pH	FILTERED REACTOR EFFLUENT pH	TOTAL ALKALINITY	TOTAL DISSOLVED CALCIUM	TOTAL DISSOLVED MAGNESIUM	TOTAL DISSOLVED ORTHO-PHOSPHATE	TOTAL DISSOLVED COD	ESTIMATED VOLATILE SOLIDS	TOTAL DISSOLVED AMMONIA
$mg\ \ell^{-1}$ (as $CaCO_3$)	-	-	$mg\ \ell^{-1}$ (as $CaCO_3$)	$mg\ \ell^{-1}$ (as $CaCO_3$)	$mg\ \ell^{-1}$ (as $CaCO_3$)	$mg\ \ell^{-1}$ (as PO_4-P)	$mg\ \ell^{-1}$ (as O)	$mg\ \ell^{-1}$	$mg\ \ell^{-1}$ (as NH_3-N)
(Effluent only)	7,71	8,07	199	105	78	4,9	82	58	10,0
(Effluent & Sludge)	9,33	9,30	233	118	103	0,8	17	12	7,6
21	9,50	9,45	243	123	103	0,5	19	13	7,4
53	9,68	9,66	247	128	103	0,4	30	21	7,5
94	9,88	9,85	230	118	99	0,3	20	14	7,6
145	10,13	10,05	193	95	87	0,2	17	12	7,4
196	10,41	10,30	168	88	70	0,1	15	11	7,8
246	10,59	10,47	138	85	41	0,1	13	9	8,3
290	10,77	10,66	120	90	21	0,1	18	13	7,9
335	10,98	11,09	119	103	8	0,1	15	11	7,7
378	11,20	11,29	138	125	4	0,1	16	11	7,7
421	11,37	11,29	166	153	4	0,1	19	13	7,9
464	11,50	11,43	198	188	4	0,1	17	12	8,7
507	11,60	11,53	224	220	4	0,1	17	12	7,9

Reaction temperature = 20-22°C; % Active lime = 78,6% (as $Ca(OH)_2$);
Settled Sewage : Total COD = 331mg ℓ^{-1}(as O); Estimated Volatile Solids = 233;
Total Kjeldabl nitrogen = 33,0mg ℓ^{-1}(as N); Total phosphorus = 6,3mg ℓ^{-1}(as P).

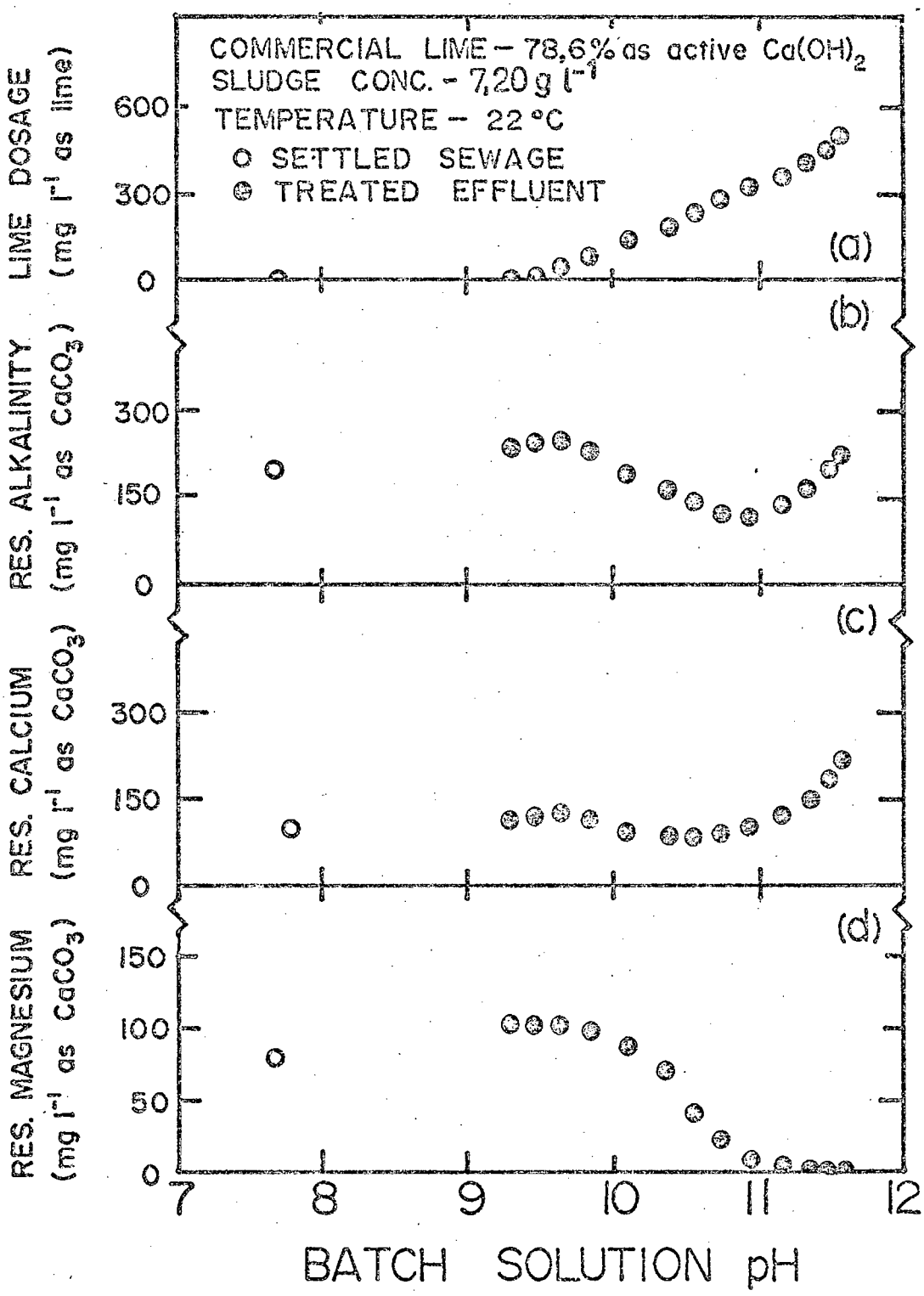


Figure 4.33 (a-d). Plots indicating the response of settled sewage to lime treatment in the presence of seed sludge (batch test)

Table 4.14

Various components contributing to the inorganic mass precipitated during lime treatment of settled sewage in the presence of inoculated seed lime-sludge (batch test)

REACTOR EFFLUENT	$CaCO_3$	LIME INSOLUBLES	$Ca_3(PO_4)_2$	$Mg(OH)_2$	INORGANIC FRACTION OF SLUDGE
9,50	15	4	22	-	41
9,68	40	11	23	-	74
9,88	93	19	23	2	137
10,13	168	30	24	10	232
10,41	228	40	24	19	311
10,59	280	51	25	36	392
10,77	320	60	25	48	453
10,98	355	70	25	55	505
11,20	380	79	25	58	542
11,37	400	88	25	58	571
11,50	410	98	25	58	591
11,60	425	107	25	58	615

All expressed as mg ℓ^{-1} (as is), except pH.

Table 4.15

Chemical composition of secondary effluent and settled sewage studied in this set of tests

Parameter/Effluent	Secondary Effluent	Settled Sewage
pH	7,64	7,71
Alkalinity (as $CaCO_3$)	163	199
Total Dissolved Calcium (as $CaCO_3$)	103	105
Total Dissolved Magnesium (as $CaCO_3$)	91	78
Total Dissolved Ortho-Phosphate (as PO_4-P)	6,2	4,9
Total Dissolved COD (as O)	25	82
Total Dissolved Ammonia (as N)	5,1	10,0
Total Phosphate (as PO_4-P)	7,0	6,3
Total COD (as O)	40	331
Total Kjeldahl Nitrogen (as N)	5,6	33

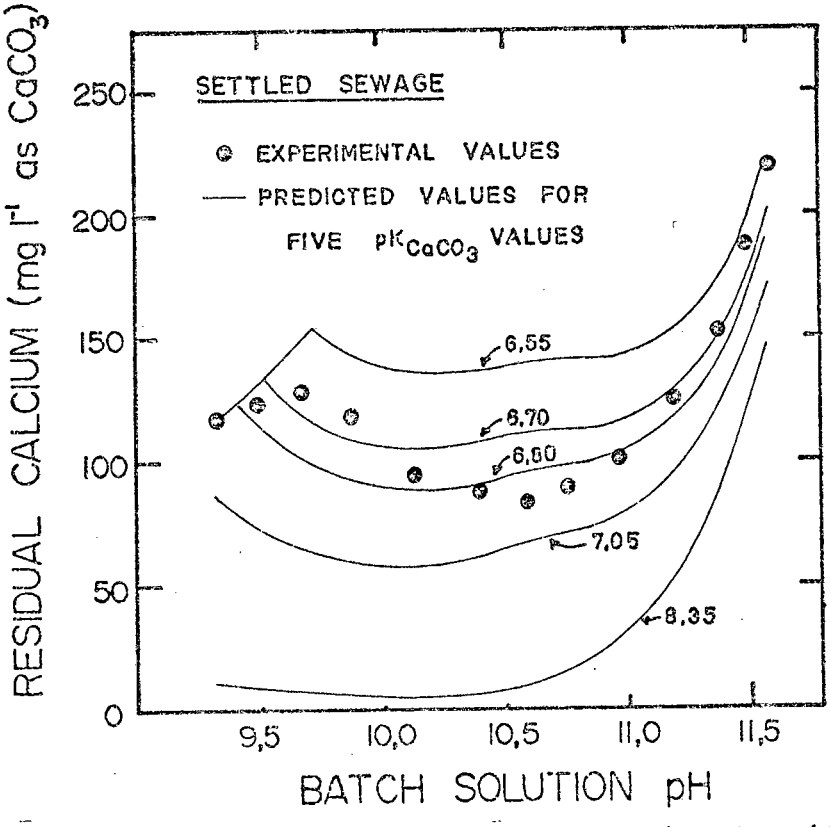


Figure 4.34. Experimental and predicted residual calcium concentration as a function of pH for lime-treated settled sewage reacted in the presence of seed lime-sludge

(3) pH range for maximum magnesium removal,

Secondary effluent - 11,0 - 11,2

Settled sewage - 11,0 - 11,2

It appears from the above results that this particular settled sewage responded similarly to lime treatment as did secondary effluent. It was therefore anticipated that the predictive models and model constants developed for secondary effluent would also hold for settled sewage.

Experimentally determined and predicted relationships for lime-treated settled sewage between residual calcium and pH are illustrated in Figure 4.34. As in the case of secondary effluent, predictions from a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 6,70 give the best average predicted Ca_T^{2+} values over the pH range studied. Predicted and experimentally

determined relationships between total alkalinity and pH, and lime dosage and pH are illustrated in Figures 4.35 (a & b), respectively. Again the correlation between predicted and experimental values is reasonable. The experimentally determined lime demand is related to the predicted lime demand by the following equation,

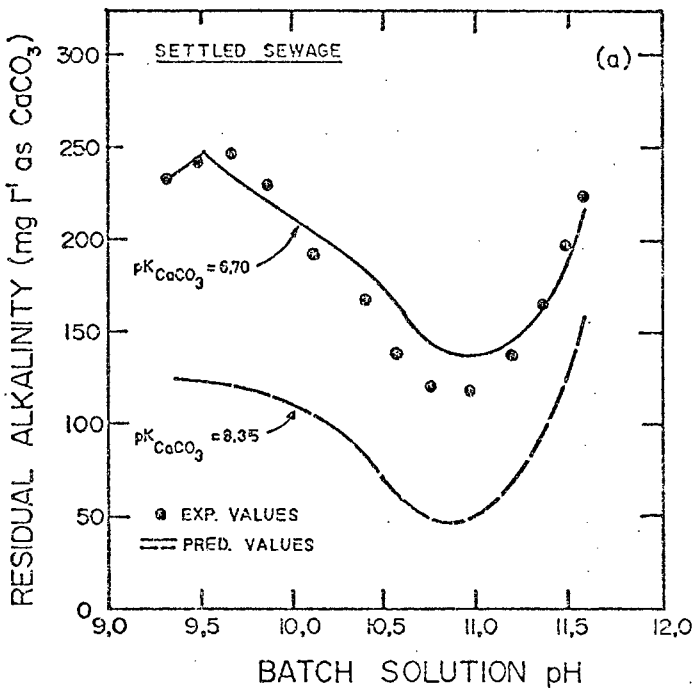
$$LD_E \simeq 1,25 \times LD_P \quad \ldots \quad (4.28)$$

Relationships between residual magnesium and pH are illustrated in Figure 4.35(c). As in the case of secondary effluent, at pH values in excess of 10,5 the relationship between Mg_T^{2+} and pH is adequately modelled by the apparent equilibrium relationship, $pK_{Mg(OH)_2'} = 10,7$. Figure 4.35(d) indicates the relationship between pH and experimentally derived and theoretically predicted masses of sludge generated.

As previously noted, the only major differences between the secondary effluent and the settled sewage were in the total organic matter concentrations (expressed as COD), i.e. 40 versus 331 mg ℓ^{-1} (as O), and in the Total Kjeldahl Nitrogen concentrations, i.e. 5,6 versus 33 mg ℓ^{-1} (as N). It is therefore concluded that these two parameters either do not play a significant role in the precipitation of $CaCO_3$ and $Mg(OH)_2$ or exert a constant effect independent of concentration in the range studied. The apparently increased $CaCO_3$ solubility for these two effluents therefore appears to result predominantly due to the presence of phosphate.

5.5 Application of Predictive Models

In the preceding sections the validity of the $CaCO_3$ and $Mg(OH)_2$ equilibrium models for predicting characterizing relationships of lime-treated effluents was demonstrated. However, this study was specific to Pretoria Sewage Works secondary effluent and settled sewage. In order to establish if these equilibrium models and their specific constants have general applicability they were applied to



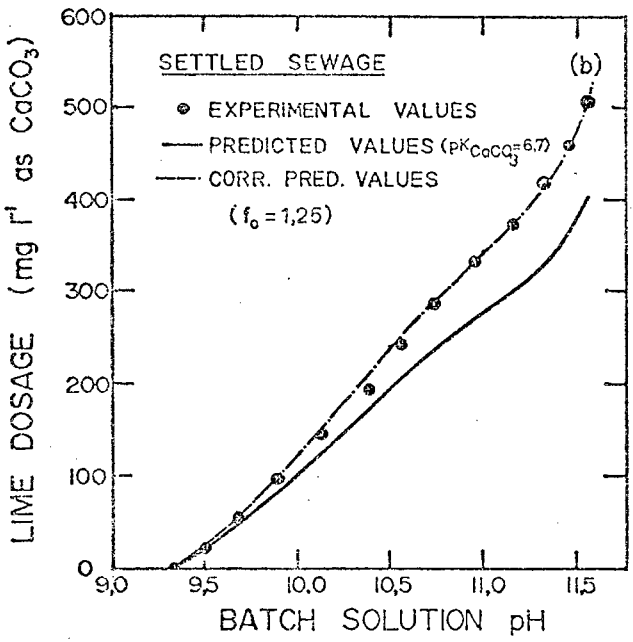


Figure 4.35 (a & b). Experimental and predicted (a) residual Alkalinity concentration and (b) lime demand as functions of pH for lime-treated settled sewage reacted in the presence of seed lime-sludge (batch test)

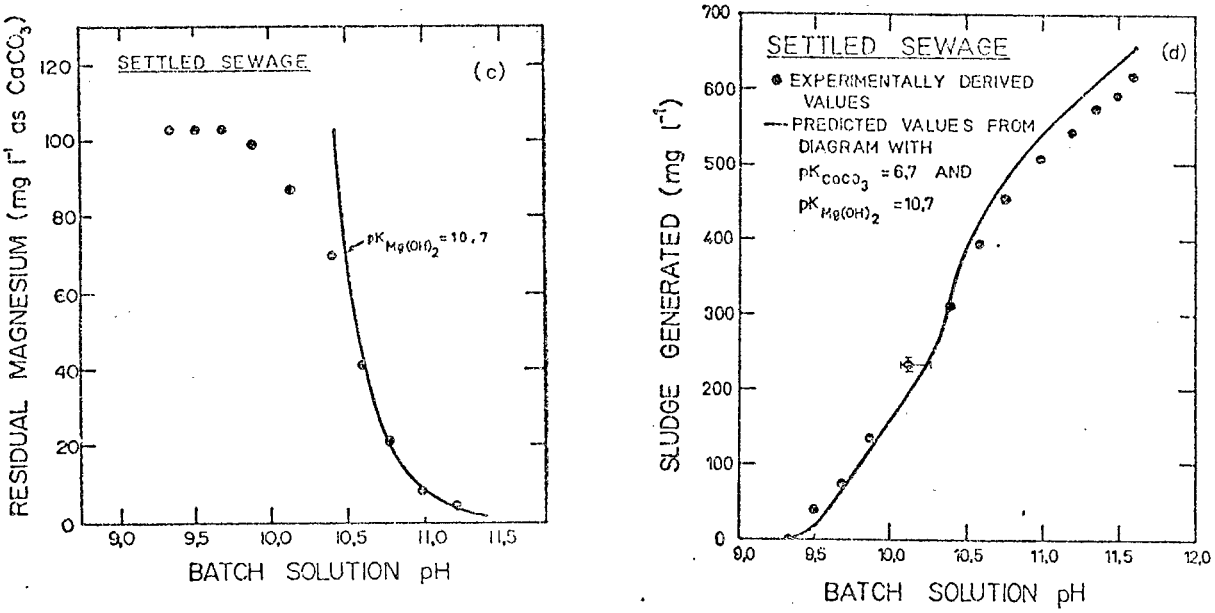


Figure 4.35 (c & d). Experimental and predicted (c) residual magnesium concentration and (d) mass of sludge generated as functions of pH for lime-treated settled sewage reacted in the presence of seed lime-sludge (batch test)

data reported in the literature for other lime-treated effluents. Two effluents are considered, i.e. secondary and raw domestic effluent.

5.5.1 Lime-treated secondary effluent

Berg, Brunner and Williams (1970) studied single stage lime clarification of secondary effluent (see Chapter 2, Section 5.2). They reported results for approximately one year's plant operation, *inter alia* residual total dissolved calcium and magnesium as functions of sludge blanket clarifier effluent pH (see Figures 4.36 (a & b)). The following average annual analysis,

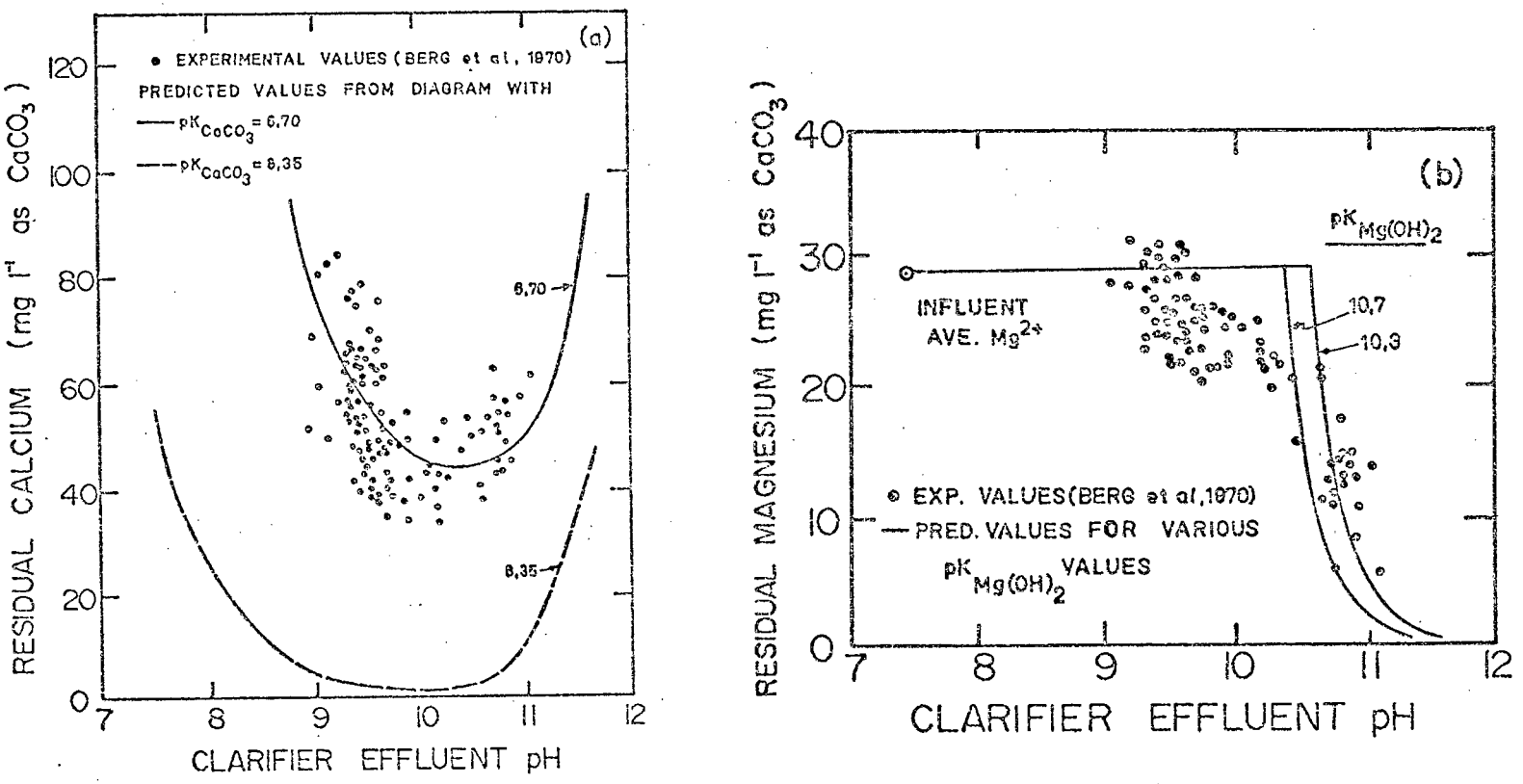


Figure 4.36 (a & b). Experimental and predicted concentrations of residual (a) calcium and (b) magnesium as functions of pH for lime-treated secondary effluent from a pilot plant.

pH - 7,5
Calcium - 256 mg ℓ^{-1} (as $CaCO_3$)
Magnesium - 115 mg ℓ^{-1} (as $CaCO_3$)
Total alkalinity - 350 mg ℓ^{-1} (as $CaCO_3$)
Temperature - 20°C

was used as a basis for predicting the relationships between residual calcium and pH. Two Modified Caldwell-Lawrence Diagrams were used for predicting the effluent quality, i.e. a Diagram with pK_{CaCO_3} = 8,35 (the thermodynamic solubility product value for calite) and another Diagram with pK_{CaCO_3} = 6,7 (the activity product constant found valid for Pretoria Sewage Works lime-treated secondary effluent).

The correlation between experimental and predicted Ca_T^{2+} values, based on the Diagram with pK_{CaCO_3} = 6,7, is excellent (see Figure 4.36(a). Two conclusions are drawn from this observation : Firstly, it appears that pK_{CaCO_3} = 6,7 is valid for two lime-treated secondary effluents of different origin irrespective of the differences in their chemical composition (see Table 4.16). This suggests that the Diagram with pK_{CaCO_3} = 6,7 may have general applicability. Obviously more lime-treated secondary effluents will have to be studied before this claim of general validity can be made.* Secondly, it was noted that although the two secondary effluents had significantly different chemical composition, specifically for Ca_T^{2+}, Mg_T^{2+} and Alkalinity, one Diagram gave excellent predictions for both effluents. This again stresses the potential value of the Diagram for predicting characterizing relationships for effluents with significantly different inorganic composition.

Prediction of residual magnesium values (Figure 4.36 (b)) using $pK_{Mg(OH)_2}$ = 10,7, which was found applicable for the Pretoria Sewage Works secondary effluent, gave fair results although a better fit to the data was ob-

*Merrill and Jorden (1975) reported a pK_{CaCO_3} of 6,8 for lime-treated secondary effluent.

Table 4.16

Chemical composition of various effluents dealt with in this discussion

Parameter	Pretoria Sewage Works		Berg *et al*	Merrill and Jorden
	Secondary Effluent	Settled Sewage	Secondary Effluent	Raw Sewage
pH	7,64	7,71	7,5	8,0
Calcium (as $CaCO_3$)	103	105	256	80
Magnesium (as $CaCO_3$)	91	78	115	30
Total alkalinity (as $CaCO_3$)	163	199	350	175
Total COD (as O)	40	331	28 (TOC*)	230
Ortho-phosphate (as P)	6,2	4,9	9,8	4,3
Ammonia (as N)	5,1	10,0	-	9

All parameters, except pH and temperature, are expressed as $mg.\ell^{-1}$;
* TOC - Total organic carbon (as C).

tained using a value of $10^{-10,3}$. A possible reason for this somewhat lower $K_{Mg(OH)_2}$ value giving better results is the lesser contact opportunity between the effluent and the sludge in the sludge blanket clarifier than was the case for the batch studies with Pretoria Sewage Work secondary effluent. It was also noted, as in the case of Pretoria Sewage Works secondary effluent, that the predictions based on a constant $K_{Mg(OH)_2}$ value break down at pH values lower than 10,5, suggesting that the controlling Mg_T^{2+} removal mechanism at these pH values is not $Mg(OH)_2$ precipitation any more.

5.5.2 Lime-treated raw domestic sewage

Merrill and Jorden (1975) studied lime treatment of raw domestic sewage from Boulder, Colorado (see Chapter 2, Section 5.2). Their experiments were conducted on a bench-scale pilot plant consisting of four reaction vessels in series (rapid mix lime addition, rapid mix $FeCl_3$ addition, rapid mix polyelectrolyte addition and flocculation) followed by a flotation unit. No sludge was recycled to the reactors and the total retention time of the reaction system was of the order of 30 minutes. Residual total dissolved calcium and magnesium values as a function of flotation unit effluent pH were reported (as illustrated in Figures 4.37 (a & b)).

Predicted relationships between residual calcium and pH, derived from three Modified Caldwell-Lawrence Diagrams with pK_{CaCO_3} values 8,35, 6,70 and 6,30 respectively, are illustrated in Figure 4.37 (a). Predictions based on $pK_{CaCO_3} = 8,35$, i.e. the thermodynamic solubility product for calcite, give very poor results. Predictions based on $pK_{CaCO_3} = 6,70$, (the activity product constant value found appropriate for Pretoria Sewage Works lime-treated secondary effluent and settled sewage and also lime-treated secondary effluent studied by Berg *et al*) give significantly improved values compared to the predictions from the Diagram based on $pK_{CaCO_3} = 8,35$. However, there is still a significant discrepancy between these predicted values and the experimentally measured values. The two major reasons for this discrepancy are probably,

(1) *Incomplete reactions* - The lime treatment of raw sewage was conducted in the absence of any recycled sludge. This mode of operation has been shown to result in incomplete reactions (Chapter 4 Section 4.4, Table 4.5).

(2) *Inhibiting substances* - Merrill and Jorden studied the lime-treatment of raw sewage, whereas the pK_{CaCO_3} values established in this study were specific for Pretoria Sewage Works secondary effluent and settled sewage. Raw sewage is expected to contain high con-

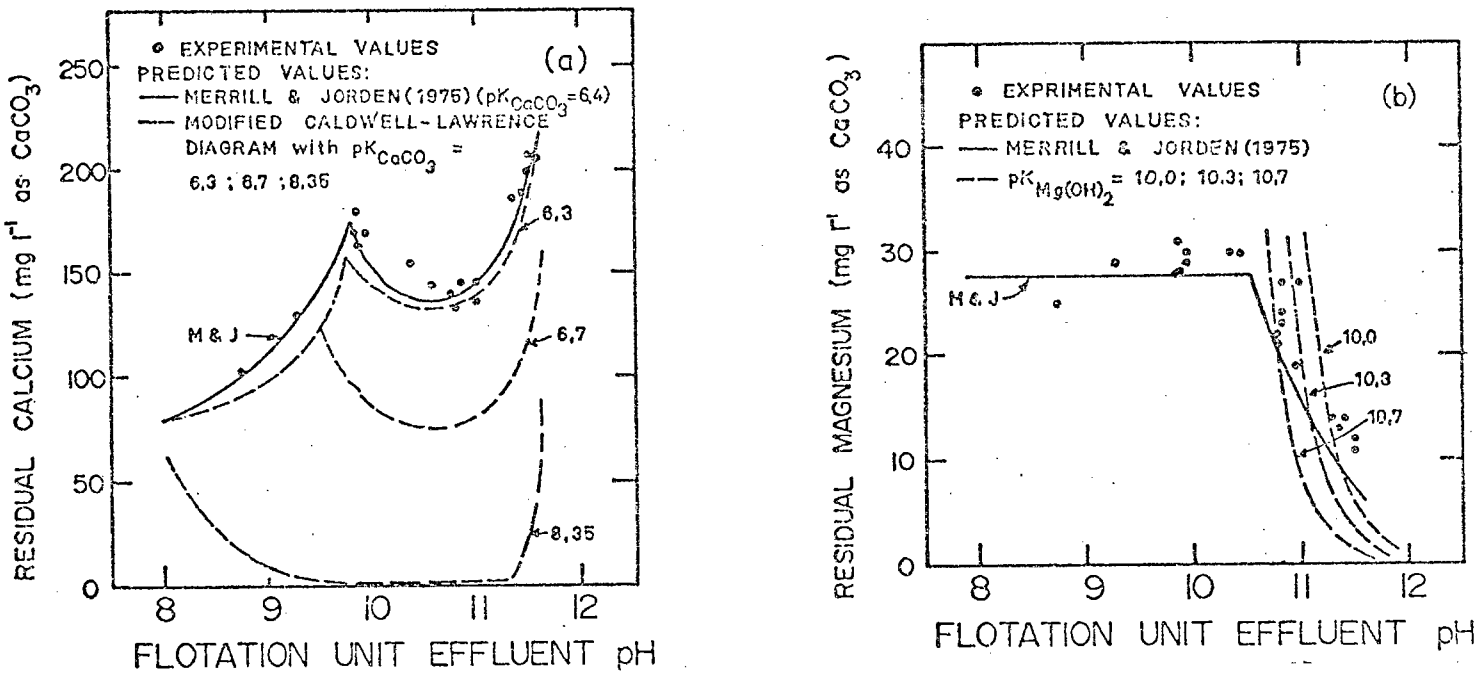


Figure 4.37 (a & b). Experimental and predicted concentrations of residual (a) calcium and (b) magnesium as functions of pH for lime-treated raw sewage from a bench-scale plant

centrations of many heterogeneous substances which may affect $CaCO_3$ precipitation and hence a different pK_{CaCO_3} may apply. Using the Modified Caldwell-Lawrence Diagram predictive technique it was possible to identify a pK_{CaCO_3} value which resulted in acceptable predicted Ca_T^{2+} values, i.e. $pK_{CaCO_3} = 6,3$ (see Figure 4.37a). This value is very close to that found by Merrill and Jorden (see Chapter 2, Table 2.2), i.e. $pK_{CaCO_3} = 6.4$.

Predicted relationships between residual total dissolved magnesium and pH are illustrated in Figure 4.37 (b). As Merrill (1974) indicated, this relationship is not adequately modelled by an equilibrium relationship with a constant solubility product. From the experimental results it appeared that the $Mg(OH)_2$ activity product is a function of pH. However, as observed in the section on lime-treated secondary effluent (Section 5.3) and also in Chapter 5, Section 2.3, the $pK_{Mg(OH)_2}$ is constant for effluents which are given sufficient reaction time in the presence of high sludge masses ($\simeq$ 10 000 mg ℓ^{-1}). The establishment of an empirical relationship for a specific effluent under specific reaction conditions, for example reaction in the absence of sludge and for short reaction times, is of limited value since such a relationship has no general validity.

From the above reported results it is concluded that equilibrium models may be used for predicting the basic relationships which characterize lime-treated effluents. Characterizing relationships for lime-treated secondary effluent from the Pretoria Sewage Works are predicted within 0 to 20 percent of the measured values when using a Modified Caldwell-Lawrence Diagram with apparent equilibrium constants $pK_{CaCO_3} = 6,70$ and $pK_{Mg(OH)_2} = 10,70$. A precondition for the validity of these constants is that adequate sludge contacting must be applied during the lime-effluent reaction and clarification phases of the process. It was demonstrated that these two constants also give reasonable predictions for lime-treated secondary effluent from a different source. Although it cannot be claimed that these constants will give reasonable predictions for all lime-treated secondary ef-

fluents, this claim does appear to have potential.

This section also demonstrated the simplicity of use of the graphical technique for predicting characterizing relationships. As may be expected, correlation between experimental and predicted values is a function of prediction model specificity. The Merrill and Jorden model which was developed to incorporate apparent solubility product constants, specifically determined for the effluent under consideration, gave somewhat better results than the generalized Modified Caldwell-Lawrence Diagram. However, it was demonstrated that the Diagram, which incorporates ion pairing effects but neglects corrections for the lime demand of ammonia, phosphates, organic matter and sludge, does give reasonable predictions which are sufficiently accurate (within 0 to 20%) for most practical purposes.

5.6 Conclusions

(1) Lime-treated effluents, both secondary treated and settled sewage, may be characterized by the inter-relationships they display between pH and lime dosage, alkalinity, residual total dissolved calcium and magnesium and sludge generated.

(2) Lime-treated secondary effluent and settled sewage display apparent solubilities for calcium carbonate and magnesium hydroxide considerably higher than those for the pure mineral forms of $CaCO_3$ and $Mg(OH)_2$, i.e. calcite and brucite. The experimentally determined activity product constants are,

$$pK_{CaCO_3} = 6,70 \quad .... \quad (9,3<pH<11,4) \quad .... \quad (4.29)$$

$$pK_{Mg(OH)_2} = 10,70 \quad .... \quad (10,5<pH<11,3) \quad .... \quad (4.30)$$

(3) Modified Caldwell-Lawrence Diagrams based on these pK values give reasonable predictions (within 0 to 20 percent) for relationships characterizing lime-treated secondary effluent and settled sewage from the Pretoria Sewage Works.

(4) Applying the Diagram with these specific constants to one instance of full-scale lime-treated secondary effluent data reported in the literature, the correlation between predicted and reported relationships between Ca_T^{2+}, Mg_T^{2+} and pH was excellent, suggesting possible general applicability. However, many more lime-treated effluents will have to be studied to substantiate this claim.

(5) It is apparent that there is a need for greater understanding of "apparent" solubility product constants of inorganic salts precipitated from lime-treated effluents.

6. GENERAL CONCLUSIONS

(1) Laboratory batch lime dissolution studies indicated the critical importance of the lime dissolution reaction in lime-waste water reaction systems. The kinetics of batch lime dissolution in Pretoria Sewage Works secondary effluent is adequately modelled by an equation proposed by Jenkins and Lee (1976),

$$-\log (1- [OH^-]/[OH^-]_\infty) = 0{,}21.t \quad \ldots\ldots \quad (4.30)$$

(2) In the batch and CSTR tests without sludge addition the calcium reactions in lime-treated secondary effluent, i.e. lime dissolution, $CaCO_3$ and $Ca_3(PO_4)_2$ precipitation, are rapid and 85 to 95 percent complete within 5 minutes reaction time. However, small but significant quantities of $CaCO_3$ (5-35 mg ℓ^{-1}) may still precipitate from solutions at reaction times of 14 minutes or longer.

(3) In batch and CSTR tests without sludge addition magnesium hydroxide precipitation from lime-treated secondary effluent is slow and for complete precipitation requires reaction times in excess of 14 minutes.

(4) In the lime treatment of secondary effluent the combined use of static mixers and sludge recirculation reduces the residence time required to produce stable effluents in CSTRs in one to two minutes.

(5) Lime-treated effluents, both secondary treated and settled sewage effluent, may be characterized by the inter-relationships displayed between the pH and lime dosage, alkalinity, residual total dissolved calcium and magnesium, and sludge generated. These relationships are adequately predicted, i.e. within 0 to 20 percent of measured values, by a Modified Caldwell-Lawrence Diagram (incorporating ion-pairing) based on the following, apparent solubility products for calcium carbonate and magnesium hydroxide,

$$pK_{CaCO_3} = 6,70 \quad .... \quad (9,3<pH<11,4) \quad .... \quad (4.31)$$

$$pK_{Mg(OH)_2} = 10,70 \quad .... \quad (10,5<pH<11,4) \quad .... \quad (4.32)$$

(6) It became apparent that there is a need for experimentally identifying pK_{CaCO_3} and $pK_{Mg(OH)_2}$ for lime-treated waste waters, effluents, surface- and ground-waters of different quality and origin and the associated application of the Modified Caldwell-Lawrence Diagram based on these constants.

(7) The laboratory studies reported in this chapter may serve as a basis for the design of lime-waste water reaction systems. However, the application of systems and models advocated in this chapter should be verified at pilot-scale level before proceeding to full-scale application.

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CHAPTER 5

LIME TREATMENT OF WASTE WATER - FULL-SCALE STUDIES

1. INTRODUCTION

Full-scale lime treatment is being applied at a number of locations, the better known plants being listed in Table 2.1 (Chapter 2). Lime treatment is usually the first unit process in a train of unit processes utilized for upgrading waste water, in some instances to drinking water quality. The well known attributes of the process such as phosphate removal, suspended, colloidal and dissolved organic material removal and clarification have been studied and repeatedly reported for full-scale plants. However, aspects relating to lime dissolution and $CaCO_3$ and $Mg(OH)_2$ precipitation have received little or no attention in these studies.

The Stander Water Reclamation Plant (Pretoria, South Africa) utilizes the lime treatment process as its first unit process in a train of unit processes for upgrading the quality of secondary effluent to drinking water standards. Operating experience with lime treatment revealed a number of problems related to the lime-effluent inorganic reactions. It was found that the lime-treated effluent was supersaturated with respect to calcium carbonate, which resulted in scale deposits in pumps and pipes transferring the effluent from one unit to the next. Internal diameters of the pipes decreased, resulting in reduced flows and eventually complete blockages. Heavy encrustations in pump casings and on pump impellers caused decreased efficiency, vibration and pump failure. Lime-treated effluents also gave rise to scale formation in the ammonia stripping tower. This resulted in maldistribution of water flow, a reduction in air flow and ultimately a lower ammonia removal efficiency. A further problem was encountered in the recarbonation of the treated effluents to give a slightly supersaturated or saturated water. The Langelier Saturation Index apparently was not applicable as waters tested in accordance with this index

were apparently undersaturated. Thus no theoretical procedure was available to predict saturated conditions from standard tests of calcium, total alkalinity and pH.

The observations above were the main reasons for initiating this study. It was argued that if a stable lime-treated effluent can be produced the aforementioned problems will be overcome. This entailed a study of the time behaviour of the lime-effluent reactions in CSTR systems. It was necessary to define stable effluents and the conditions for producing them. Laboratory studies on these problems have been reported in the previous two chapters. It now remains to be established if the findings of the laboratory studies are applicable to full-scale systems.

In the study of $CaCO_3$ and $Mg(OH)_2$ precipitation in the full-scale lime treatment process the following specific objectives were set, to :

(1) Evaluate the precipitation phenomena in a full-scale plant, with and without sludge recirculation, over a range of lime dosage rates and reactor retention times.
(2) Compare effluent response to lime treatment in a full-scale plant with the response measured in the laboratory bench-scale plant.
(3) Obtain the optimum configuration, operating conditions and lime dosage rates for the Stander Plant lime process reactor - clarifier system.
(4) Predict process effluent quality from simple influent characterization tests, utilizing the Modified Caldwell-Lawrence Diagram.

2. LIME-EFFLUENT REACTIONS - IN THE ABSENCE OF RECIRCULATED SLUDGE

Full-scale studies of the lime-effluent reactions were commenced by studying the reactions in the lime reactor on the Stander Plant without sludge recirculation. In this set of experiments the lime slurry was added in-line to the influent ahead of the lime reactor; the mixture discharged into the lime reactor where it was agitated by means of air

sparging; the reactor effluent was discharged to the primary clarifier; sludge from the clarifier underflow was recirculated to the clarifier inlet. These tests are comparible with the laboratory CSTR tests for the lime treatment of secondary eflfuent without sludge addition (see Chapter 4, Section 4), except that in the laboratory test mechanical stirring was the mode of reactor solution mixing.

2.1 Lime Reaction System

The original plant design was influenced by the requirement for synthetic detergent removal. For this purpose a foam fractionator was included in the unit process train. However, at the time the plant was commissioned there was a change over from hard to soft detergents and the secondary treated effluent detergent concentration fell to such low levels that foam fractionation was no longer necessary. While the foam fractionation process was necessary the lime was added to the effluent flow after the fractionator and this reaction mixture flowed directly into the sludge blanket clarifier flocculation compartment. When foam fractionation was no longer necessary the foam fractionator was converted to a lime reactor, the lime being added prior to the reactor. The air sparging system which was used for producing foam in the foam fractionator was retained in the lime reactor for mixing the lime slurry with the influent. The lime slurry was added in-line to the influent pipe, but no static mixers were used. The lime reactor system is shown in Figure 5.1. For basic design information on the lime reactor and sludge blanket clarifier see Table 5.1 and Figure 5.2, respectively.

2.2 Experimental Procedure

The lime treatment process as described above was operated continuously for a period of two weeks for this set of tests. Twenty sets of samples of secondary effluent, reactor effluent and lime slurry were drawn from the relevant streams during this period. Each specific test was conducted as follows : The lime dosage rate was manually adjusted to give a preselected pH in the reactor. This pH was allowed to

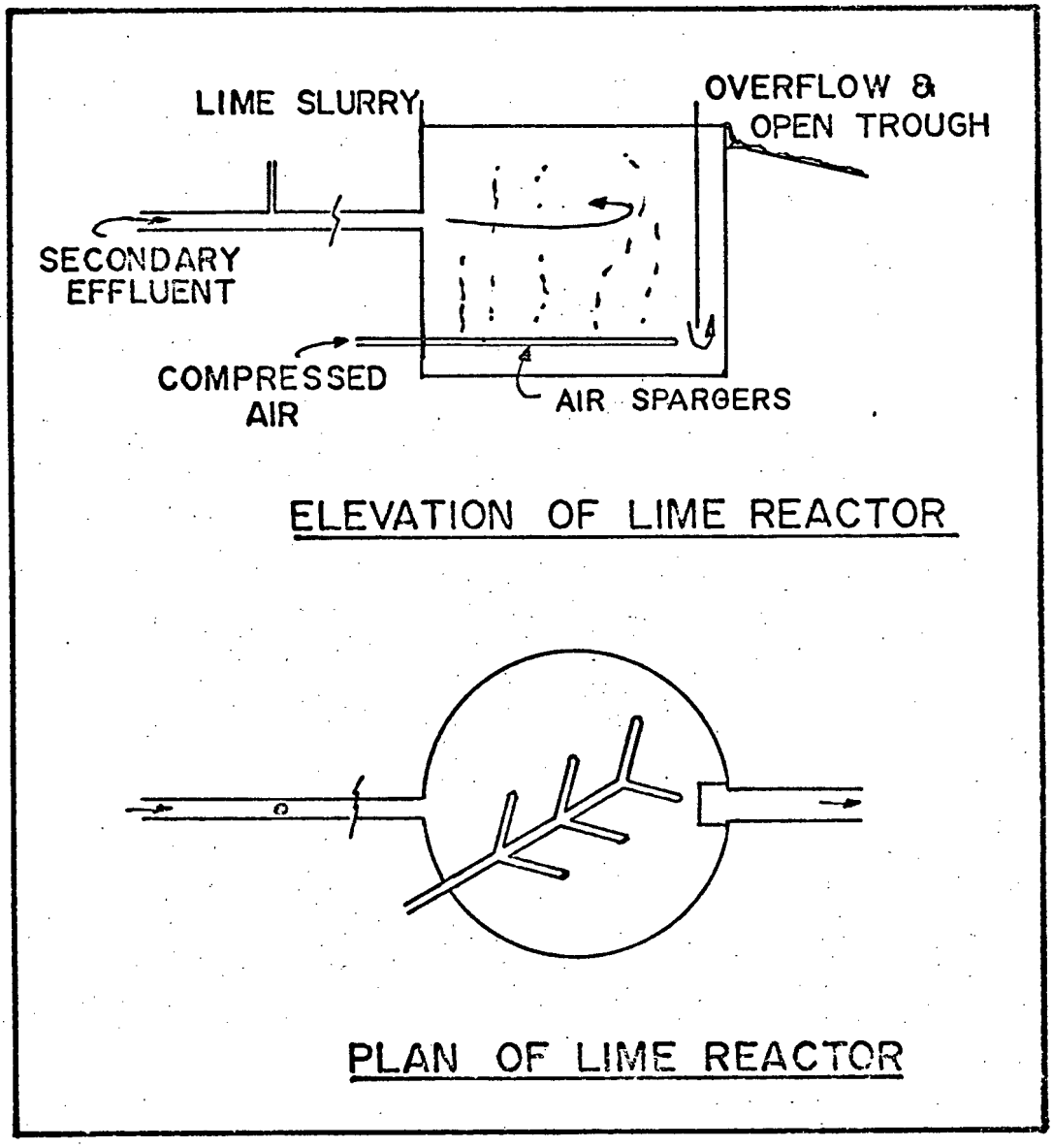
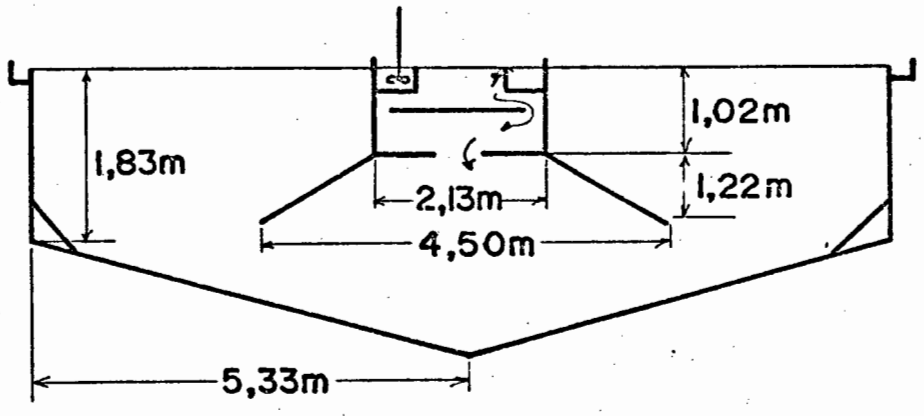


Figure 5.1. Full-scale lime reactor (Pre - 1975, without sludge recirculation)



Volume of flocculation compartment	-	32,9 m^3
Volume of clarifier	-	206.0 m^3
Design flow	-	4,5 $M\ell\ d^{-1}$
Retention time - flocculation comp.	-	10,5 min
- clarifier	-	66 min
Overflow rate	-	5,65 $m^3/m/h$
Upflow rate	-	2,38 m/h
Surface loading rate	-	0,632 $m^3/m^2/h$
Lime flow rate from floc. cone	-	0,439 m/min

Figure 5.2. Stander Plant primary clarifier design details

Table 5.1

Stander plant lime reactor - design details

Dimensions :	Diameter	- 4,88 m
	Water head	- 3,02 m
	Water volume	- 56,5 m^3
Base flow		- 4 500 m^3/day
Hydraulic retention time		- 18,1 min
Mechanical stirrer -	Power	- 15 hp
	Stirrer revolutions	- 96,7 rpm
Raw water feed pipe diameter		- 20,3 cm
Linear flow rate		- 40,4 cm sec^{-1}
Static mixer**	No. of segments	- 6
	Diameter	- 20,3 cm
	Length (total)	- 1,22 m

stabilize, usually requiring minor adjustments to the lime dosage rate. The system was run for approximately three reactor residence times (3 x 10,8* minutes) under stabilized pH conditions, after which the samples were drawn. The lime dosage rate was then adjusted to give a different preselected reactor pH and the procedure repeated. Lime-effluent reactions were studied in a pH range of 10,8 to 11,5.

The parameters analysed during this investigation are listed in Table 5.2. Reactor effluent sample post precipiation was quenched by rapid vacuum filtration through Whatman No. 542 filter paper and by

*It was noted that the mean residence time, determined by tracer studies, was considerably lower than the hydraulic retention time, i.e. 10,8 and 18,1 minutes, respectively. This indicates that the air-sparging system resulted in poor mixing.

**Static mixing was used only in experiments described in Sections 3 and 4.

Table 5.2

Analyses performed on various streams of the lime treatment process

	STREAM SAMPLES				
Parameter	HTE (1)	LS (2)	RE (3)	RS (4)	CO (5)
Temperature	x		x		x
pH	x		x		x
Total Alkalinity	x		x		x
Dissolved Calcium*	x		x		x
Dissolved Magnesium*	x		x		x
Dissolved Orthophosphate*	x		x		x
Dissolved COD*	x		x		x
Dissolved NH_3-N*	x		x		x
Dissolved NO_3-N*	x				
Dissolved Sodium*	x				
Dissolved Potassium*	x				
Dissolved Chlorides*	x				
Dissolved Sulphates*	x				
Total Calcium	x		x		x
Total Magnesium	x		x		x
Total Ortho-phosphate	x		x		x
Suspended Solids			x	x	
Total solids		x			

*Concentration of substances filtered through Whatman No. 42 (or 542)

HTE(1) - Humus tank effluent
LS(2) - Lime slurry
RE(3) - Reactor effluent
RS(4) - Recycled sludge stream
CO(5) - Clarifier overflow

filtrate acidification. Sample preparation and the sequence of analysis for reactor influent and effluent are shown in Figure 5.3. Estimates for lime dosage and masses of $CaCO_3$, $Mg(OH)_2$ and $Ca_3(PO_4)_2$ precipitated were calculated as follow :

$$\text{Lime dosage (mg } \ell^{-1}) = \frac{\text{L.S.F. x LS}}{\text{E.F.}} \quad \ldots\ (5.1)$$

where L.S.F. - Lime slurry flow rate (ℓ min^{-1})
LS - Lime slurry concentration (mg ℓ^{-1})
E.F. - Effluent flow rate (ℓ min^{-1})

$$CaCO_3(ppt) = (Ca_T - Ca_T^{2+} - 1{,}94 \times PO_{4_{Ca}}) \times 2.50 \quad \ldots\ (5.2)$$

where $CaCO_3(ppt)$ - Calcium carbonate precipitated (mg ℓ^{-1} as $CaCO_3$)
Ca_T - Total calcium (mg ℓ^{-1} as Ca)
Ca_T^{2+} - Total dissolved calcium (mg ℓ^{-1} as Ca)
$PO_{4_{Ca}}$ - Ortho-phosphate precipitated as $Ca_3(PO_4)_2$ (mg ℓ^{-1} as PO_4-P)

$$Mg(OH)_2(ppt) = (Mg_T - Mg_T^{2+}) \times 4.12 \quad \ldots\ (5.3)$$

where $Mg(OH)_2(ppt)$ - Magnesium hydroxide precipitation (mg ℓ^{-1} as $CaCO_3$)
Mg_T - Total magnesium (mg ℓ^{-1} as Mg)
Mg_T^{2+} - Total dissolved magnesium (mg ℓ^{-1} as Mg)

$$Ca_3(PO_4)_2(ppt) = (PO_{4T} - PO_{4T}^{3-}) \times 5{,}00 \quad \ldots\ (5.4)$$

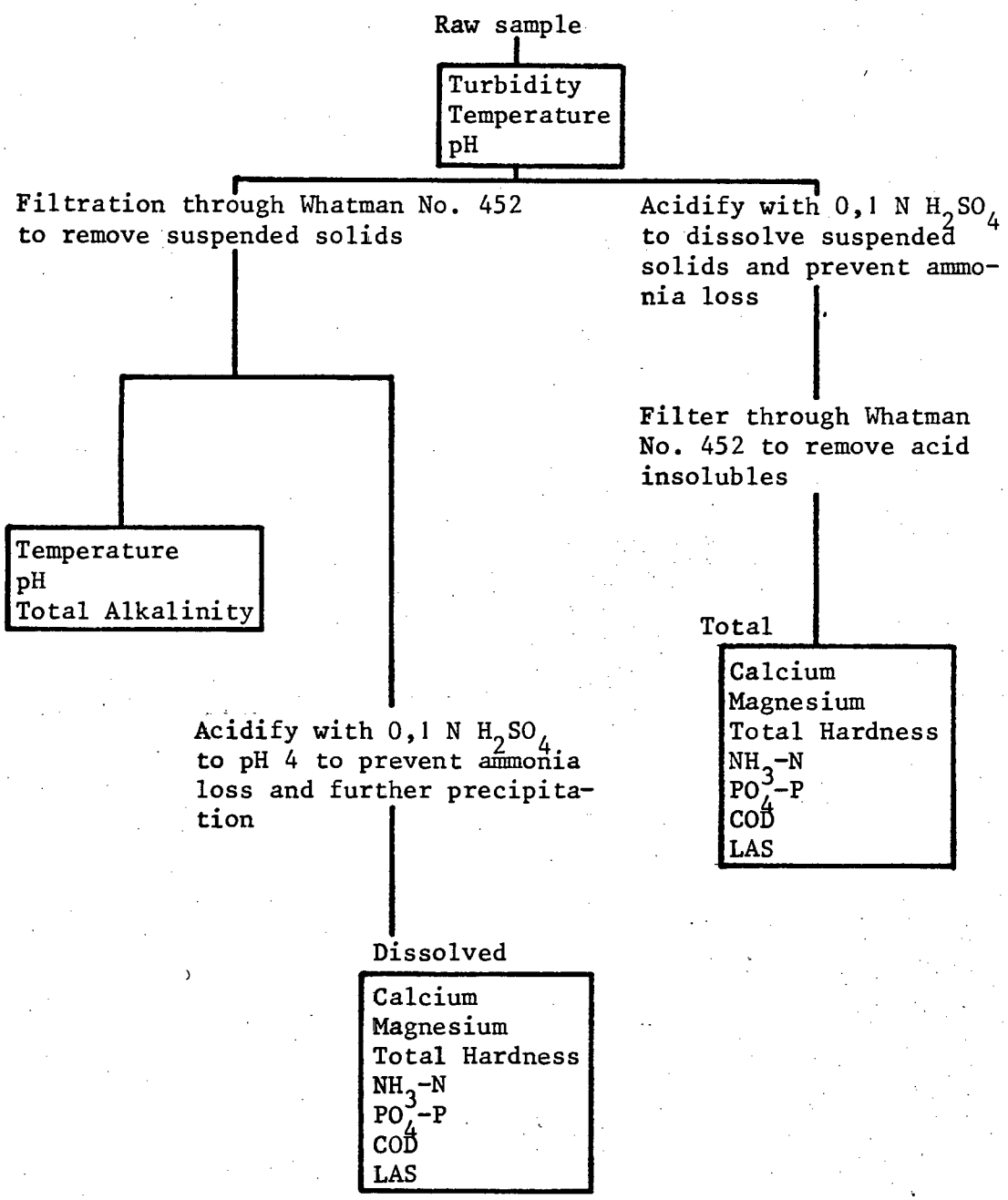


Figure 5.3 Sample preparation and analysis procedure

where $Ca_3(PO_4)_2$ (ppt) - Tricalcium phosphate precipitated (mg ℓ^{-1})
PO_{4T} - Total ortho-phosphate (mg ℓ^{-1} as P)
PO_{4T}^{3-} - Total dissolved ortho-phosphate (mg ℓ^{-1} as P)

Raw data collected during this investigation are listed in Appendix 14.

In this chapter reference will be made to the term *sludge age* (or sludge retention time) in the system. The term sludge age is commonly associated with the activated sludge process, but is also useful in the context of inorganic precipitation where precipitate (sludge) is removed from the treated water in a sludge blanket clarifier and is recirculated to the influent stream to act as seed for the precipitation reactions. Sludge age is defined as,

$$R_S = \frac{\text{Mass of sludge in the system}}{\text{Mass of sludge wasted per day}} \quad \ldots\ldots \quad (5.6)$$

and is a measure of the average time the sludge generated by precipitation is retained in the system, i.e. the reactor and clarifier. For practical aspects related to the sludge age concept see Chapter 7, Section 3.4.2.

2.3 Results and Discussion

Typical experimental results are listed in Table 5.3. Plots characterizing the lime-treated effluent, i.e. pH versus lime dosage, total alkalinity, and residual total dissolved calcium and magnesium are illustrated in Figure 5.4(a-d). Although this series of full-scale tests is comparible with the laboratory CSTR tests for lime-treating secondary effluent at a mean residence time of 7,5 minutes, there are a number of differences between the two sets of experiments, i.e. differences in secondary effluent quality and temperature (Table 5.4), mode of mixing in the reactor (mechanical versus air mixing), reactor design and reaction temperature.

Lime dosage vs pH

The relationship between lime dosage and reactor effluent pH is illustrated in Figures 5.4(a) and 5.5. The scatter of experimental data points about the smooth curve through the data points in Figure 5.5 is primarily due to quality variations in the secondary effluent (Table 5.4), i.e. the Alkalinity varied between 122 and 170 mg ℓ^{-1} (as $CaCO_3$). For comparison, the experimental results obtained for the lime dosage versus pH relationship for laboratory CSTR studies are also shown in Figure 5.5. Here a lime dosage of 360 (350 - 370) mg ℓ^{-1} lime (as $CaCO_3$) was required to establish the control pH of 11,2. This dosage is substantially lower than the dosage required on the full-scale plant. This discrepancy is attributed primarily to the increased lime demand on the full-scale plant due to the reaction of lime with carbon dioxide in the sparger air. The air flow rate in the air sparging system was 7 m^3 air min^{-1} ($\equiv$ 2,2 m^3/air/m^3 effluent, or 300 mg CO_2/litre effluent*).

An estimate of the quantity of lime lost in reaction with CO_2 may be calculated from the following equation,

$$ACID_{LTSE} = ACID_{HTE} + Mg(OH)_2(ppt) - L.D. + CO_2(RE) \quad .... \quad (5.5)$$

Where $ACID_{LTSE}$ = Acidity of lime-treated secondary effluent (mg ℓ^{-1} as $CaCO_3$)

$ACID_{HTE}$ = Acidity of secondary effluent (mg ℓ^{-1} as $CaCO_3$)

$Mg(OH)_2(ppt)$ = Magnesium hydroxide precipitated (mg ℓ^{-1} as $CaCO_3$)

L.D. = Lime dosage (mg ℓ^{-1} as $CaCO_3$)

$CO_2(RE)$ = Carbon dioxide reacted with effluent (mg ℓ^{-1} as $CaCO_3$)

*Air contains approximately 0,03% CO_2 (v/v) $\equiv$ 135 mg CO_2 (as $CaCO_3$) per litre air.

Table 5.3

Typical analyses for lime-treated secondary effluent from the Stander Plant lime reactor

LIME DOSAGE	REACTOR EFFLUENT pH	TOTAL DISSOLVED CALCIUM	TOTAL DISSOLVED MAGNESIUM	TOTAL ALKALINITY	RESIDUAL ORTHO-PHOSPHATE	DISSOLVED COD	AMMONIA	SUSPENDED SOLIDS
$mg\ \ell^{-1}$	-	$mg\ \ell^{-1}$ as $CaCO_3$	$mg\ \ell^{-1}$ as $CaCO_3$	$mg\ \ell^{-1}$ as $CaCO_3$	$mg\ \ell^{-1}$ as PO_4-P	$mg\ \ell^{-1}$ as O	$mg\ \ell^{-1}$ as NH_3-N	$mg\ \ell^{-1}$
310	10,80	125	52	159	<0,1	24	3,5	225
316	11,20	144	41	164	<0,1	23	2,5	256
384	11,10	181	31	181	<0,1	23	5,1	301
441	11,20	188	26	188	<0,1	23	4,9	334
501	11,30	206	10	212	<0,1	24	6,3	359
633	11,46	256	5	260	<0,1	25	7,6	383

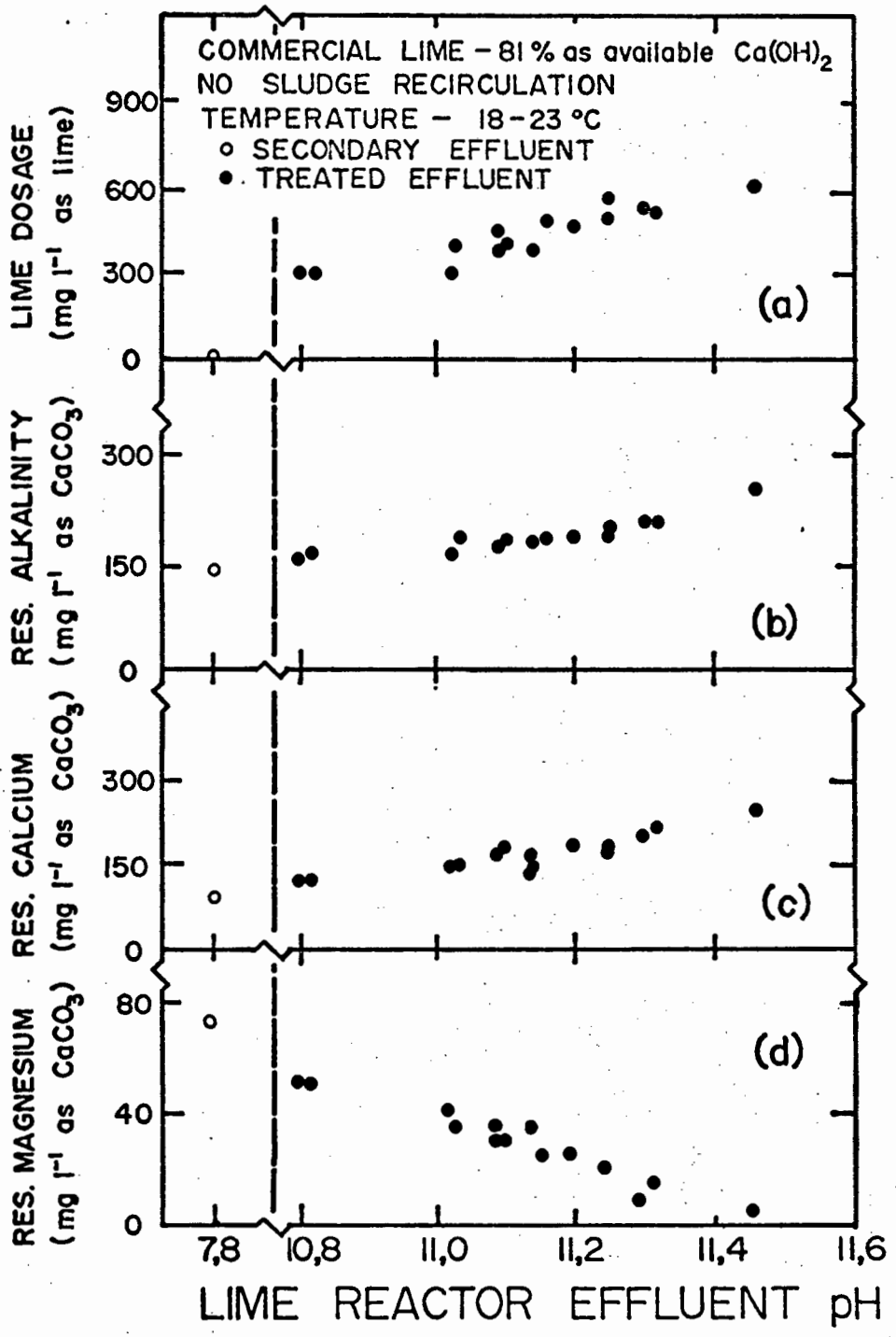


Figure 5.4(a-d). Secondary effluent response to lime treatment in the full-scale Stander Plant lime reactor (June, 1974).

Table 5.4

Comparison between the quality of secondary effluent treated in the laboratory and full-scale tests

Parameter	Secondary Effluent			
	Laboratory Tests		Full-Scale Tests	
	Average	(Min-Max)	Average	(Min-Max)
Temperature (^{o}C)	20,0	(19,0-21,0)	20,9	(19,0-22,8)
pH	-	(7,74-7,90)	-	(7,65-8,06)
Total Alkalinity (as $CaCO_3$)	193	(175-200)	144	(122-170)
Calcium (as $CaCO_3$)	108	(100-123)	90	(83-100)
Magnesium (as $CaCO_3$)	82	(78-84)	73	(67-78)
Ortho-Phosphate (as PO_4-P)	7,3	(6,0-8,7)	6,3	(5,1-7,9)
COD (as O)	37	(28-60)	38	(30-46)
Ammonia (as NH_3-N)	10,0	(7,8-12,0)	7,4	(3,1-14,6)

Since all the terms excepting the CO_2 term are known, an estimate of the mass of carbon dioxide which reacted with the effluent may be made using Eq. (5.5). Such a set of estimates for CO_2 absorbed versus pH are illustrated in Figure 5.6. It appears from this graph that at pH values of 11,4 or higher, the air is nearly completely stripped of all its carbon dioxide (0,03% v/v ≡ 135 mg CO_2 (as $CaCO_3$) per litre air). Consequently the carbon dioxide absorbed from the air will constitute a significant lime demand (150 -300 mg ℓ^{-1} as $CaCO_3$) at pH 10,8 to 11,4. The addition of calcium ions thus added will react with the CO_3^{2-} ions formed from the CO_2 in the air to give precipitation of additional masses of $CaCO_3$, i.e. the sludge generation rate is increased. To eliminate this source of lime wastage the air sparging system was replaced by a mechanical stirrer. Tests using this mode of reactor solution agitation are reported in Section 4 of this Chapter.

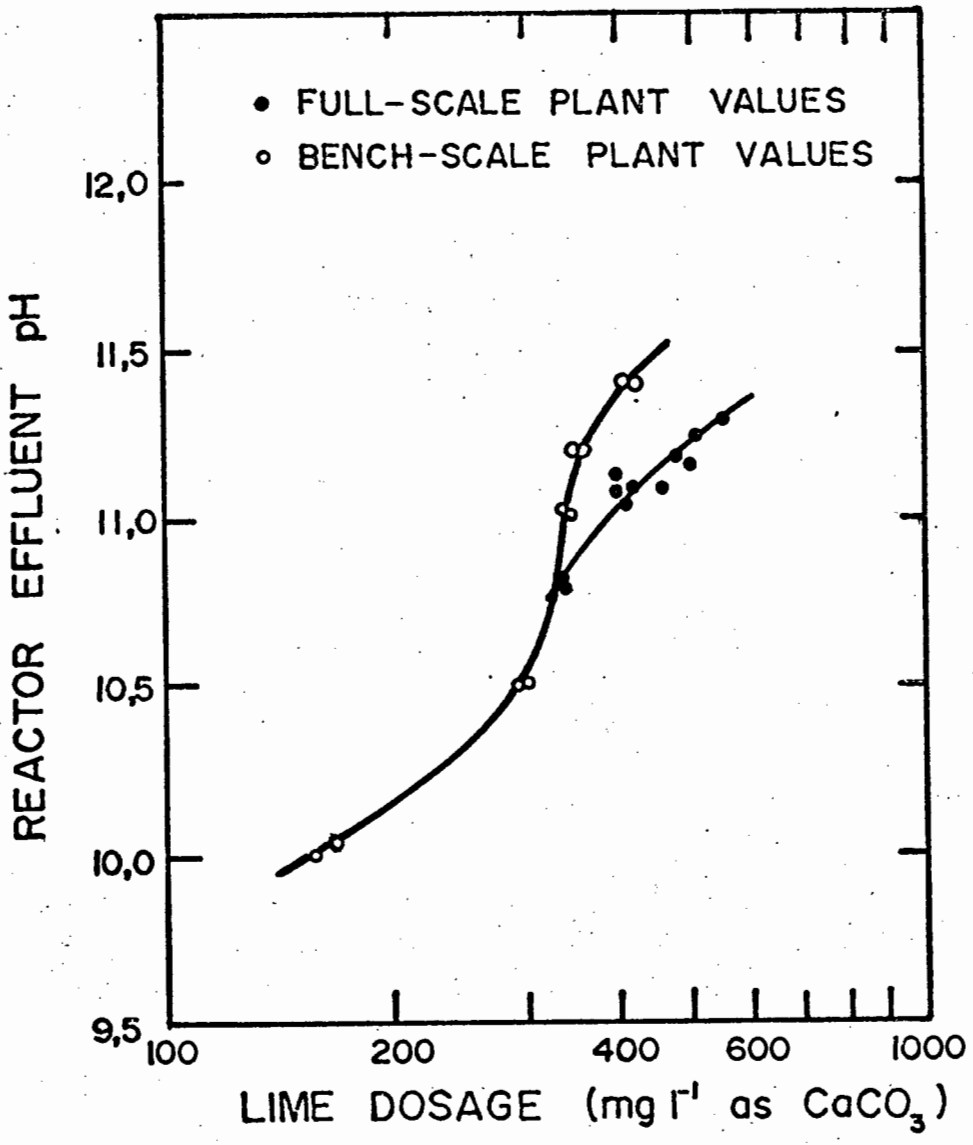


Figure 5.5. Relationship between lime dosage and treated effluent pH for Pretoria Sewage Works secondary effluent

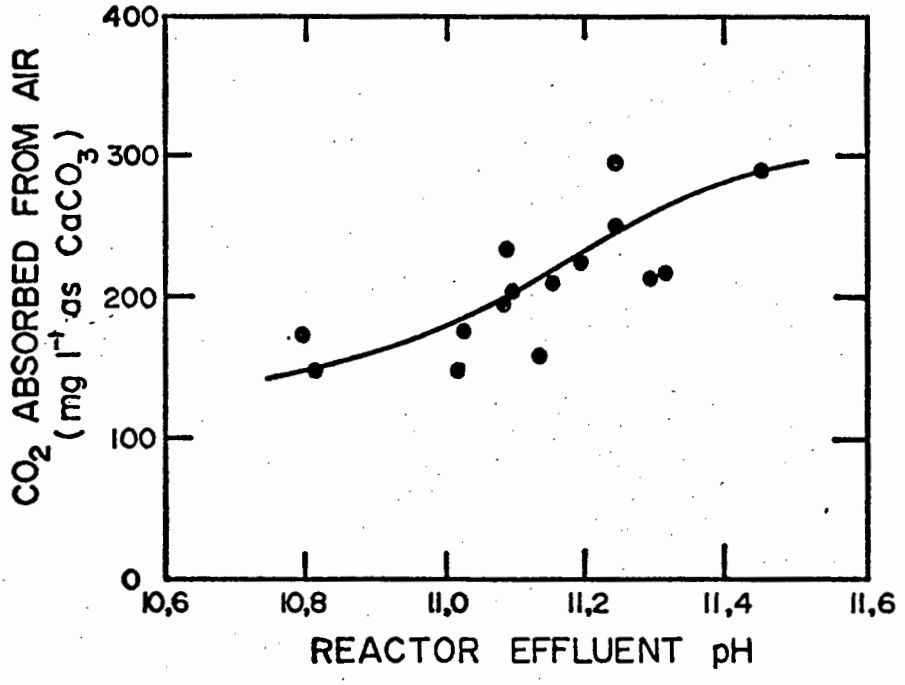


Figure 5.6. Estimated quantities of CO_2 absorbed by alkaline effluent from the air used for agitation in the lime reactor

Sludge production vs pH

The masses of calcium carbonate, magnesium hydroxide and tricalcium phosphate precipitated as a function of pH, were calculated using Eqs. (5.2, 5.3 and 5.4) and are listed in Table 5.5. Experimentally determined concentrations of suspended solids in the reactor effluent are also listed in Table 5.5. The two sets of results are consistent, although the measured suspended solids concentrations are on average 10% lower than the calculated values.

Table 5.5

Concentrations of inorganic salts precipitated on lime addition to secondary effluent in the Stander Plant lime reactor

Reactor Effluent pH	Calcium Carbonate Precipitated	Magnesium Hydroxide Precipitated	Tri-Calcium Phosphate Precipitated	Calculated mass of inorganics generated	Measured Suspended Solids
	mg ℓ^{-1} (as $CaCO_3$)	mg ℓ^{-1} (as $Mg(OH)_2$)	mg ℓ^{-1} (as $Ca_3(PO_4)_s$)	mg ℓ^{-1}	mg ℓ^{-1}
10,80	221	12	27	260	225
10,82	223	12	26	261	211
11,02	226	18	27	271	256
11,14	269	21	36	326	290
11,09	212	21	35	268	255
11,03	320	24	28	372	345
11,10	257	27	33	317	301
11,09	289	27	33	349	302
11,20	297	30	38	365	334
11,16	301	24	30	335	296
11,25	319	30	41	390	344
11,32	312	33	40	385	337
11,30	339	36	29	404	359
11,25	391	33	32	456	369
11,46	288	39	28	355	383

Residual calcium vs pH

Experimental results for residual total dissolved calcium as a function of pH are plotted in Figure 5.7 together with results for the laboratory CSTR experiments. Also shown are the predicted Ca_T^{2+} versus pH relationships, based on the average analysis of the secondary effluent listed in Appendix 15 and using Modified Caldwell-

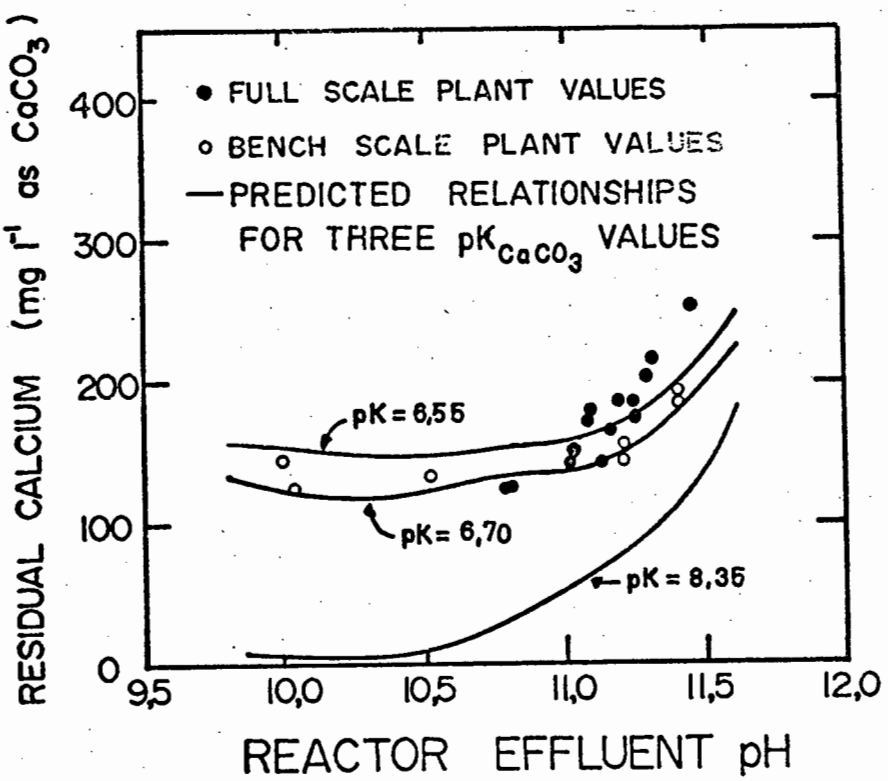


Figure 5.7. Relationship between residual calcium concentration and pH for lime-treated secondary effluent from the full-scale plant lime reactor (no sludge recirculation)

Lawrence Diagrams with pK_{CaCO_3} = 8,35; 6,70; and 6,55; temperature = 20°C; μ = 0.015. For pK_{CaCO_3} = 6,70 the correlation between experimental and predicted Ca_T^{2+} versus pH relationships for laboratory CSTR lime-treated secondary effluent is fair. However, the predictions are less good for the full-scale lime reactor effluent results, the correlation deteriorating with increasing pH, i.e. the predictions are within 15 mg ℓ^{-1} at pH 10,80, but only within 70 mg ℓ^{-1} (as $CaCO_3$) at pH 11,45. One of the reasons for the poor fit probably was the adsorption of carbon dioxide introduced into the reactor by the air sparger method of mixing, with associated higher lime demand.

Residual magnesium versus pH

Typical experimental results for residual total dissolved magnesium as a function of pH are illustrated in Figure 5.8. Magnesium removal in the full-scale CSTR system was considerably more effective than in the laboratory CSTR system. As indicated in the section on laboratory studies (Chapter 4, Section 4), magnesium removal in the absence of recycled sludge is very sensitive to the specific precipitation conditions. At pH values greater than 11,0 the magnesium hydroxide activity products were approximately constant (see Figure 5.9), i.e.

$$p(APC[Mg(OH)_2]) = -\log ([Mg_T^{2+}][OH^-]^2) = 9,9 \quad .... \quad (5.7)$$

where APC = Activity Product Constant

This value is considerably lower than the value found for bench-scale $Mg(OH)_2$ precipitation in the presence of sludge, i.e. pAPC = 10,70. indicating the crucial importance of sludge for the $Mg(OH)_2$ precipitation reaction.

Effect of lime treatment on PO_4, COD and NH_3

Full-scale and laboratory CSTR systems gave results very similar to each other for removal of ortho-phosphate, COD and NH_3 (compare Tables 4.4 and 5.6). Ortho-phosphate removal was complete (<0,1 mg ℓ^{-1} as PO_4-P) for all the pH values studied (10,80 - 11,46). Partial removal of dissolved COD (34-46 percent) and NH_3 removal (12 - 24 percent) was also observed in this pH range. These removals are pH independent at pH values greater than 10,8.

Stability of lime-treated effluent

The stability of effluents produced in the full-scale lime reactor (mean residence time = 10,8 $\pm$ 1,9 minutes at design flow) was tested by placing 1ℓ treated effluent samples in sealed glass bottles and allowing an additional 24 hours batch reaction time. Typical results for pH, Ca_T^{2+} and Mg_T^{2+} are listed in Table 5.7. It is evident from these results that the effluent is not stable with respect to both the calcium

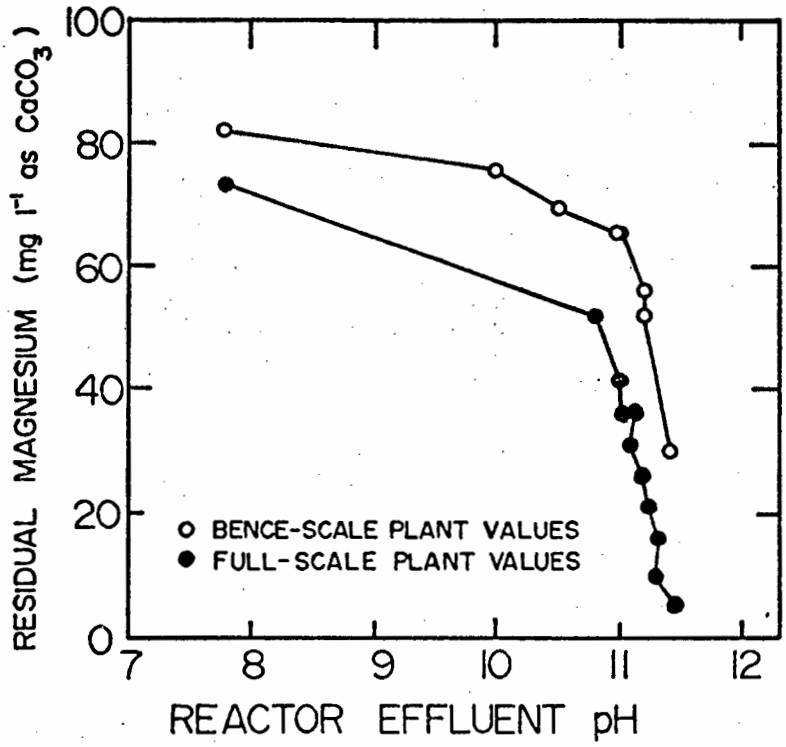


Figure 5.8. Residual magnesium concentration as a function of pH for lime-treated secondary effluent from two CSTR systems (no sludge recirculation)

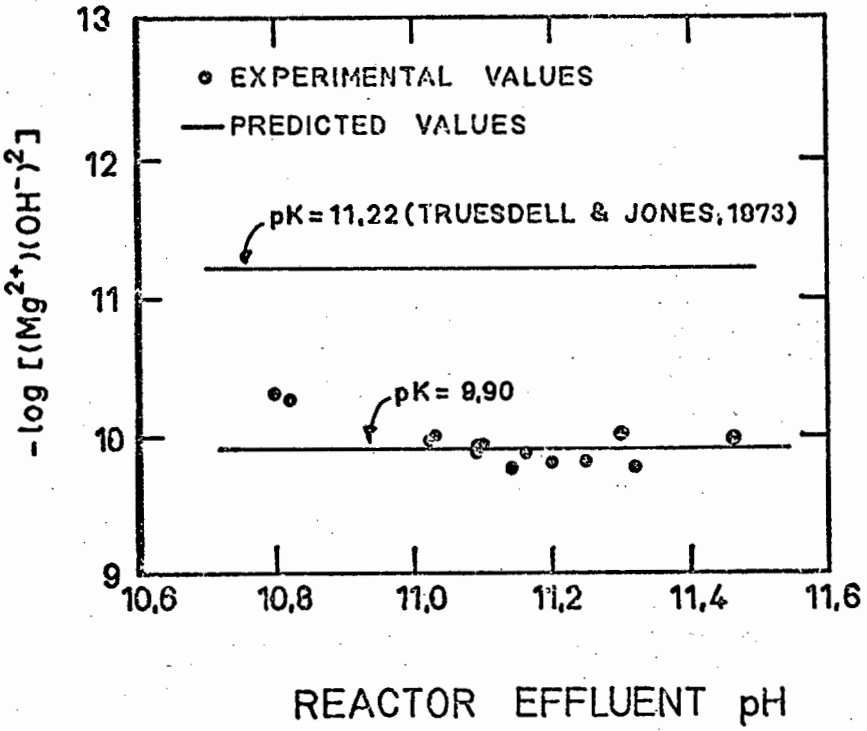


Figure 5.9. Plot indicating the independence of $Mg(OH)_2$ activity product values from pH for lime-treated secondary effluent from the Stander Plant lime reactor (no sludge recirculation)

Table 5.6

Ortho-phosphate, COD and ammonia removal in the full-scale lime reactor*

Secondary Effluent pH	Treated Effluent pH	Ortho-Phosphate	COD	Ammonia
-	-	mg ℓ^{-1} (as PO_4-P)	mg ℓ^{-1} (as O)	mg ℓ^{-1} (as NH_3-N)
7,87	-	5,3	30	4,5
-	10,80	<0,1	24	3,5
7,92	-	5,4	33	3,1
-	11,02	<0,1	23	2,5
7,82	-	7,6	35	7,3
-	11,20	<0,1	23	4,9
7,88	-	5,5	39	8,5
-	11,46	<0,1	25	7,6

*Sets of corresponding secondary effluent and treated effluent are listed above.

and magnesium reactions. Up to 25 mg ℓ^{-1} (as $CaCO_3$) calcium carbonate and 31 mg ℓ^{-1} (as $CaCO_3$) magnesium hydroxide still precipitated from the reactor effluent over a period of 24 hours. This is consistant with observations made on the stability of effluents produced in analagous laboratory CSTR studies.

2.4 Conclusions

With regard to full-scale lime treatment studies without sludge addition the following conclusion can be drawn :

Table 5.7

Stability of lime-treated effluents produced in the full-scale lime reactor with no sludge recirculation*

CSTR Reaction Time		Batch Reaction Time	Effluent pH	Residual Total Dissolved Calcium	Residual Total Dissolved Magnesium
min.		hours	-	mg ℓ^{-1} (as $CaCO_3$)	mg ℓ^{-1} (as $CaCO_3$)
10,8		-	11,05	175	36
10,8	+	24	10,98	150	5
10,8		-	11,29	188	21
10,8	+	24	11,31	169	5
10,8		-	11,26	219	16
10,8	+	24	11,32	206	5

*Corresponding sets of results for CSTR and Batch reactor effluents are listed above.

(1) Mixing by air sparging in the full-scale lime reactor resulted in carbon dioxide absorption from the air by the alkaline effluent. This resulted in the ineffective use of lime and higher sludge production rates.

(2) The relationship between residual total dissolved calcium and pH can be estimated by means of a Modified Caldwell-Lawrence Diagram with $pK_{CaCO_3} = 6,7$.

(3) The residual total dissolved magnesium - pH relationship for lime-treated secondary effluent may be predicted by using an apparent activity product constant,

$$p(APC[Mg(OH)_2]) = 9,9 \quad .... \quad 11,0<pH<11,5 \quad .... \quad .... \quad (5.8)$$

(4) Ortho-phosphate removal to concentrations less than 0,1 mg ℓ^{-1} (as P), partial dissolved COD (34 - 46 percent) and ammonia (12 - 24 percent) removal were observed in the pH range 10,8 - 11,5.

(5) Studies of the stability of the effluent demonstrated that this effluent was not stable - significant quantities of calcium carbonate and magnesium hydroxide were precipitated, i.e. upto 25 and 31 mg ℓ^{-1} (as $CaCO_3$), respectively, when the reactor contents was allowed to react for a further 24 hours.

3. LIME-EFFLUENT REACTIONS - IN THE PRESENCE OF RECIRCULATED SLUDGE

The investigation reported in the previous section indicated that lime-treated secondary effluent produced in a full-scale reactor system with 10,8 minutes mean residence time and no sludge recirculation, was not stable. Laboratory studies reported in Chapter 4, Section 4, indicated that sludge inoculation into the reacting mixture resulted in stable effluents at short CSTR residence times. For this reason a study was made on the full-scale plant utilizing sludge recirculation to the reactor in an effort to obtain optimal results.

3.1 Experimental Design

In formulating an experimental design the following questions were asked,

(1) When employing sludge recirculation, is it necessary to have a reactor before discharge to the sludge blanket clarifier, or is the reaction opportunity in the sludge blanket clarifier sufficient to produce a stable effluent?

(2) If a reactor appears to be necessary, should the point of the sludge addition be prior or subsequent to the reactor; if prior, the problem of inhibition of lime dissolution may be present; if subsequent, the sludge necessary as seed for the precipitation reactions is absent from the reactor.

To investigate these alternatives the following operational modes were tested (see Figure 5.10),

(1) Lime reactor and sludge blanket clarifier, with sludge recirculation prior to the reactor,
(2) Lime reactor and sludge blanket clarifier, with sludge recirculation subsequent to the reactor, and
(3) Sludge blanket clarifier only, with sludge recirculation.

These three modes of operation were tested over a period of twelve days. A series of tests were performed as follows : The pH was kept constant at a particular preselected value in the reactor over a period of three days and the three modes of plant operation were evaluated each over a one day period. Four reactor control pH values were studied, i.e. 10,8; 11,0; 11,2 and 11,4. The reactor contents were mixed by air sparging. The sludge recirculation rate was kept constant at 10 percent of the plant flow and the sludge concentration in the underflow from the sludge blanket clarifier was maintained in the range 50-80 g ℓ^{-1}, because these values gave the best sludge blanket stability. The sampling procedures, analyses and data reduction were as described in Section 2.2. Analyses of the influent (secondary effluent), lime reactor effluent and clarifier overflow are listed in Appendix 15.

3.2 Results and Discussion

Experimental results for residual total dissolved calcium as a function of sludge blanket clarifier effluent pH are illustrated in Figure 5.11. There appear to be no major differences in Ca_T^{2+} for the different modes of operation.

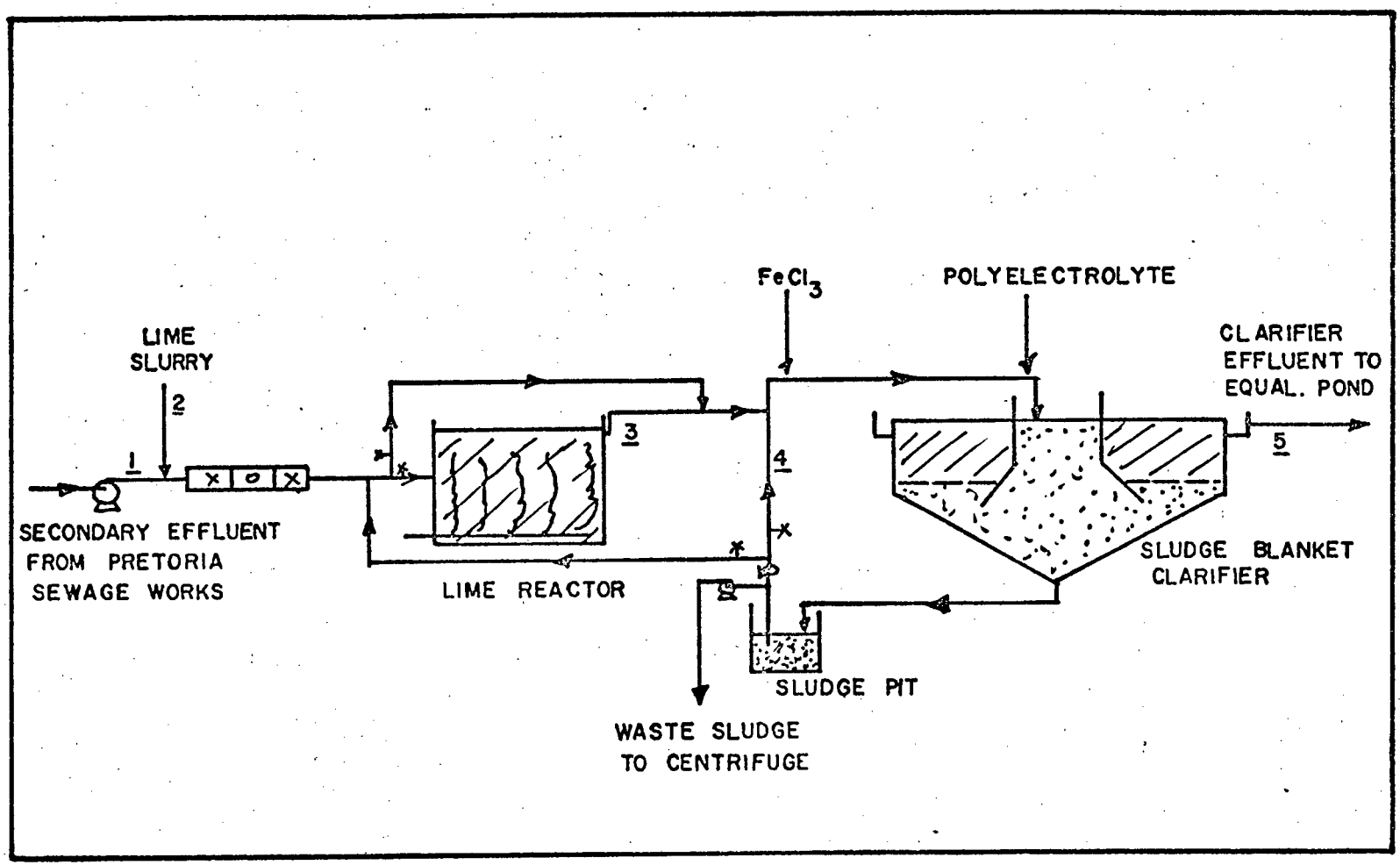


Figure 5.10. Schematic diagram indicating piping and valves installed for operating three different modes of lime treatment

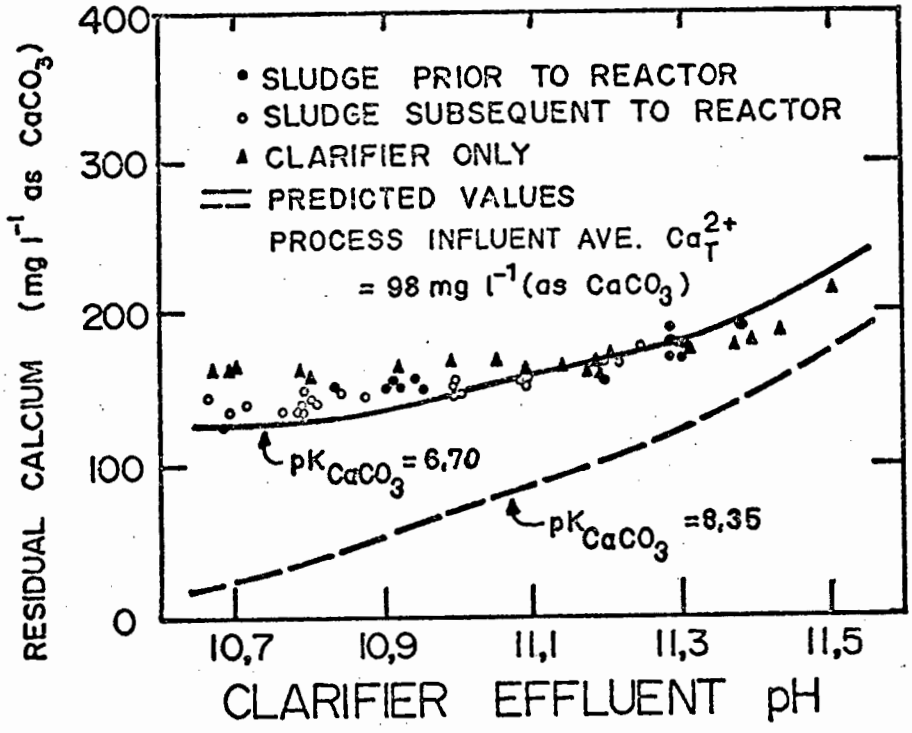


Figure 5.11. Relationships between residual calcium concentration and pH for three modes of full-scale plant lime treatment process operation

However, at the same pH values in the range 10,6 to 11,2, it appears that using a reactor prior to the clarifier (irrespective of whether sludge addition preceded or followed the reactor) gives slightly lower Ca_T^{2+} values (10-25 mg ℓ^{-1} as $CaCO_3$) than when using the clarifier only. This implies the production of a more stable effluent when using a reactor prior to a sludge blanket clarifier.

In order to determine if it is possible to predict the effluent quality theoretically, prediction of Ca_T^{2+} values as a function of effluent pH were made by means of a Modified Caldwell-Lawrence Diagram. For prediction purposes the following average *influent* quality was used :

pH = 7,5; Ca_T^{2+} = 98 mg ℓ^{-1}(as $CaCO_3$); Mg_T^{2+} = 70 mg ℓ^{-1}(as $CaCO_3$); total alkalinity 130 mg ℓ^{-1}(as $CaCO_3$); temperature = 20°C; total dis-

solved solids = 600 mg ℓ^{-1}. The predicted Ca_T^{2+} versus pH relationship from a Diagram with pK_{CaCO_3} = 6,70 is in good agreement with the experimentally determined values (see Figure 5.11). (In passing it should be noted that the effluent Ca_T^{2+} is higher than in the influent).

Experimental results for residual total dissolved magnesium, Mg_T^{2+}, as a function of pH are illustrated in Figure 5.12. There are distinct differences between the results for the three different modes of operation. Significantly improved results are indicated by the results from the reactor - sludge blanket clarifier combinations compared to the clarifier only. With regard to sludge discharge to the process stream prior or subsequent to the reactor, the results show marginal improvement for discharge prior to the reactor. It therefore appears that mode 1, i.e. reactor plus sludge blanket clarifier with sludge recirculation prior to the reactor, gives the best results. For this mode it appears that (1) the extended exposure of the treated effluent to the sludge resulted in the lowest Mg_T^{2+} values in clarifier effluent

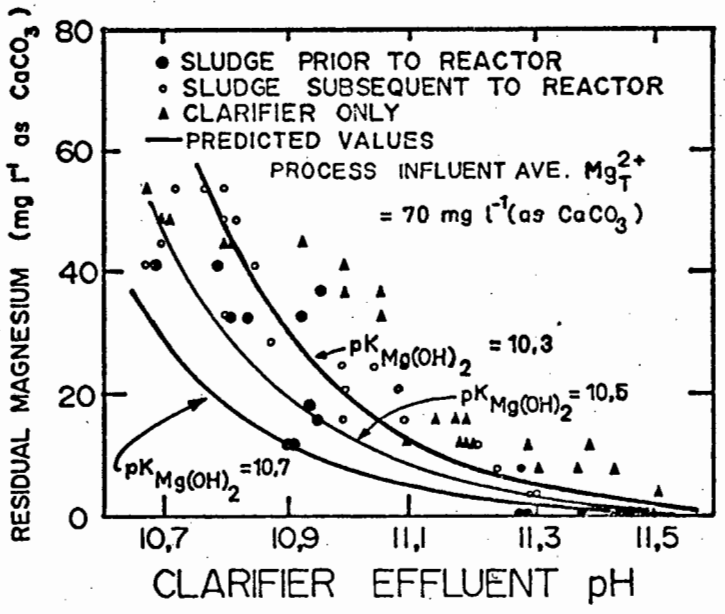


Figure 5.12. Relationships between residual magnesium concentration and pH for three modes of full-scale plant lime treatment operation

at any particular pH and (2) the magnesium residuals were adequately predicted by using $pK_{Mg(OH)_2} = 10,5$.

In mode 1 both calcium and magnesium residuals were reduced by an additional 10-20 mg ℓ^{-1} (as $CaCO_3$) in the pH range 10,8 - 11,4 in comparison with mode 3. Although these additional reductions may appear not significant in comparison to the overall masses of calcium and magnesium removed from solution, these additional removals indicate a closer approach to equilibrium, i.e. near completion of the slow secondary phase precipitation reactions (see Chapter 4, Section 4). Although this set of tests indicated the best mode of operation, unfortunately samples were not taken of the effluent from the reactor, so that the relative contributions of the reactor and the sludge blanket clarifier could not be evaluated. The relative contributions of these two unit processes are investigated in Section 4.

3.3 Conclusions

Three modes of lime treatment were evaluated on the Stander Plant,

(a) Mode 1 - Lime reactor and sludge blanket clarifier, with sludge recirculation prior to the reactor.

(b) Mode 2 - Lime reactor and sludge blanket clarifier, with sludge recirculation subsequent to the reactor.

(c) Mode 3 - Sludge blanket clarifier only, with sludge recirculation.

(1) It was found advantageous to incorporate a reactor before the sludge blanket clarifier and to recirculate sludge to a point prior to the reactor (mode 1). This mode of operation resulted in the lowest calcium and magnesium residuals. The poorest results were obtained when using only the sludge blanket clarifier (mode 3). With respect to Ca_T^{2+} the differences between the three modes were marginal, but with respect to Mg_T^{2+} the improvement in additional reduction in mode 1 over mode 3 was of the order 10-20 mg ℓ^{-1} Mg (as $CaCO_3$).

(2) Mode 1 effluent Ca_T^{2+} versus pH relationships may be predicted by using a Modified Caldwell-Lawrence Diagram with $pK_{CaCO_3} = 6,7$.

(3) Mode 1 effluent Mg_T^{2+} versus pH relationship may be predicted by using $pK_{Mg(OH)_2} = 10,5$.

4. LIME-EFFLUENT REACTIONS - AT LONG REACTOR AND CLARIFIER RESIDENCE TIMES

A number of alterations were made to the lime treatment process at the end of 1974. The air-sparging mixing system in the lime reactor was replaced by a mechanical stirrer (11,2 kW, 97 rpm). A more reliable lime slurry dosing system and improved closed-loop pH control over the lime addition were installed. Scale formation in the pipes transporting the lime-treated effluent reduced the plant flow from 4,5 Mℓ d^{-1} to 2,4 Mℓ d^{-1}. Thus the reactor clarifier residence times increased approximately two times compared to those maintained at normal plant flow. Also, as the sludge concentration was maintained constant at the old value, the sludge age increased about two times. These changed conditions gave an unexpected opportunity to investigate the effect of increased residence time and sludge age (i.e. increased contact opportunity) on $CaCO_3$ and $Mg(OH)_2$ precipitation in the full-scale plant.

The evaluation was conducted over a period of seven days. Sludge was recirculated prior to the reactor on the first three days and subsequent to the reactor on the last four days. Samples of influent, reactor effluent and clarifier overflow were taken approximately every 2 to 3 hours, four sets of samples being taken every day. The lime dosage was varied to result in clarifier overflow pH values ranging from 10,8 to 11,7.

Sample preparation and analysis were as outlined in Section 2.2. Detailed analyses of the influent to lime reactor (secondary effluent) and clarifier overflow are listed in Appendix 16.

4.1 Results and Discussion

Total dissolved calcium, Ca_T^{2+}, as a function of pH for lime reactor effluent and clarifier overflow is shown in Figures 5.13 and 5.14, respectively. From the results it does not appear that sludge recirculation prior to the reactor has a significant effect on the reactor effluent Ca_T^{2+} values. Clarifier overflow Ca_T^{2+} values are very similar to those for the *lime reactor* effluent and it therefore appears that there is no significant calcium removal in the clarifier, i.e. the calcium removal was already complete in the reactor.

The Ca_T^{2+} versus pH relationship for clarifier effluent was predicted using the following influent analysis : pH = 7,70; Ca_T^{2+} = 96 mg ℓ^{-1} (as $CaCO_3$); Mg_T^{2+} = 80 mg ℓ^{-1} (as $CaCO_3$); temperature = 20°C; total dissolved solids = 600 mg ℓ^{-1}, and a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 6,7. The predicted values are in excellent agreement with the experimental data (Figure 5.14). Comparing the predicted relationships and experimental results in Figure 5.14 and Figure 5.10, it appears that doubling residence times and sludge age gives slightly improved results, although it is difficult to quantize the effects as the influent quality to the plant also changed (see pH, total alkalinity and calcium values for secondary effluent in Appendix 16).

Effluent residual magnesium concentrations, Mg_T^{2+}, as a function of pH for the reactor and clarifier are shown in Figures 5.15 and 5.16, respectively. With regard to magnesium removal, firstly the removal in the reactor was incomplete and more so when the sludge was added subsequent to the reactor (see Figure 5.15). For the whole system, i.e. reactor plus sludge blanket clarifier, the degree of Mg_T^{2+} removal appears to be independent of whether the sludge was recycled prior or subsequent to the reactor (see Figure 5.16). $Mg(OH)_2$ precipitation in the clarifier appears to correct for any deficiency in precipitation prior to this unit process. Comparing the "reactor plus clarifier" mode results (Figure 5.16) with those for the same mode of operation but with shorter sludge age (Figure 5.12), it appears

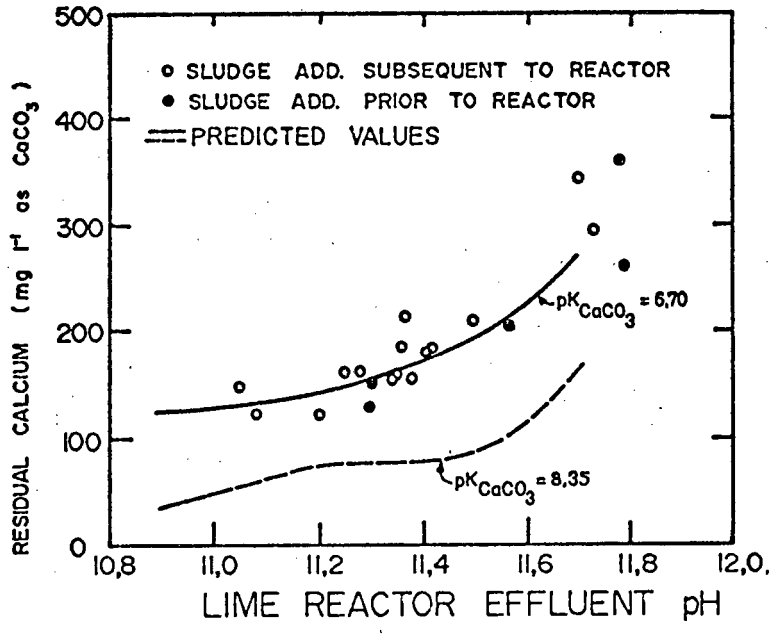


Figure 5.13. Lime reactor effluent residual calcium concentration as a function of pH for long retention time and sludge age

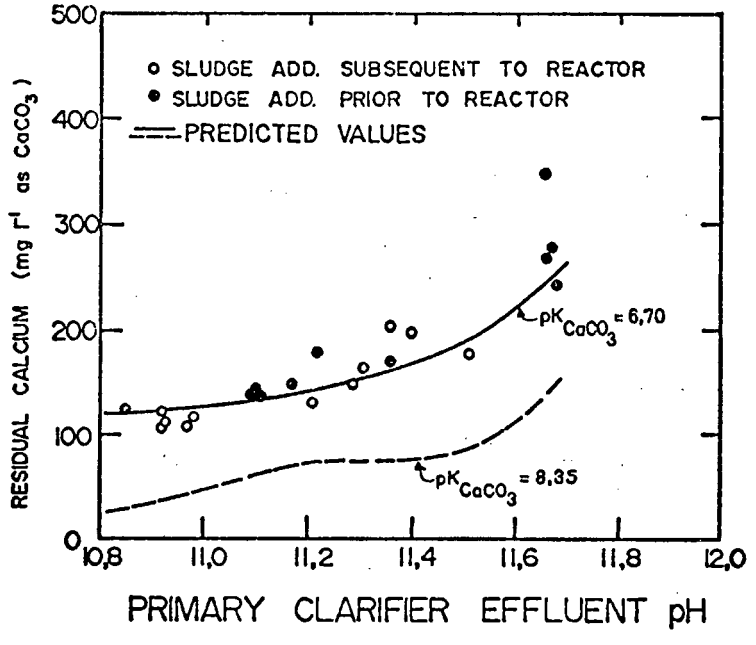


Figure 5.14. Primary clarifier effluent residual calcium concentration as a function of pH for long retention time and sludge age

that doubling the effluent retention time and sludge age resulted in slightly improved effluent quality.

Prediction of residual magnesium as a function of pH using $pK_{Mg(OH)_2}$ = 10,5 resulted in an excellent fit to the experimental data Figure 5.16. This $pK_{Mg(OH)_2}$ value is lower than that obtained in the batch test, i.e. pK = 10,7 (see Figure 4.35), but higher than that obtained by Berg, Brunner and Williams (1970), i.e. pK = 10,3. In the tests with no sludge recirculation (see Figure 5.9) the experimental $pK_{Mg(OH)_2}$ value was 9,9. It is concluded from these results that the degree of completeness of $Mg(OH)_2$ precipitation is sensitive to the contact opportunity (effluent residence time and sludge age) and that under full-scale plant design conditions (as set out in Chapter 7) a $pK_{Mg(OH)_2}$ value of 10,3 to 10,5 can be expected to operate.

It is also apparent from the above results that the longer the contact time between sludge and effluent, i.e. the longer the sludge age, the more complete will be the $CaCO_3$ and $Mg(OH)_2$ precipitation reactions. However, there is an upper limit to the sludge age in high lime processes – in the literature it is reported that at high pH values and long exposure times hydrolysis of the organic matter in the sludge results in increased clarifier COD concentrations. In the case of the Stander Plant, operating at pH values between 11,2-11,4, sludge ages of not longer than 3-6 days are recommended (Van Vuuren and Wiechers, 1971).

4.2 Conclusions

(1) Compared to removals at standard residence times, increasing the lime reactor and sludge blanket clarifier residence times by a factor of two did not result in any increased calcium removal, but in a slight increase in magnesium removal.

(2) For the standard residence time the Ca_T^{2+} versus pH, and Mg_T^{2+} versus pH relationships can be adequately predicted using a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 6,7 and $pK_{Mg(OH)_2}$ = 10,3 to 10,5 respectively.

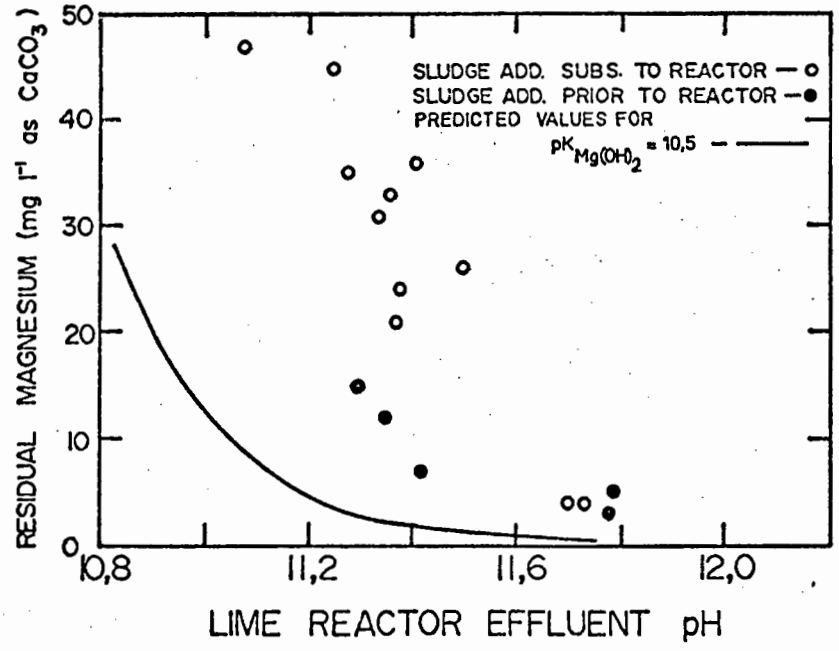


Figure 5.15. Lime reactor effluent residual magnesium concentration as a function of pH for long retention time and sludge age

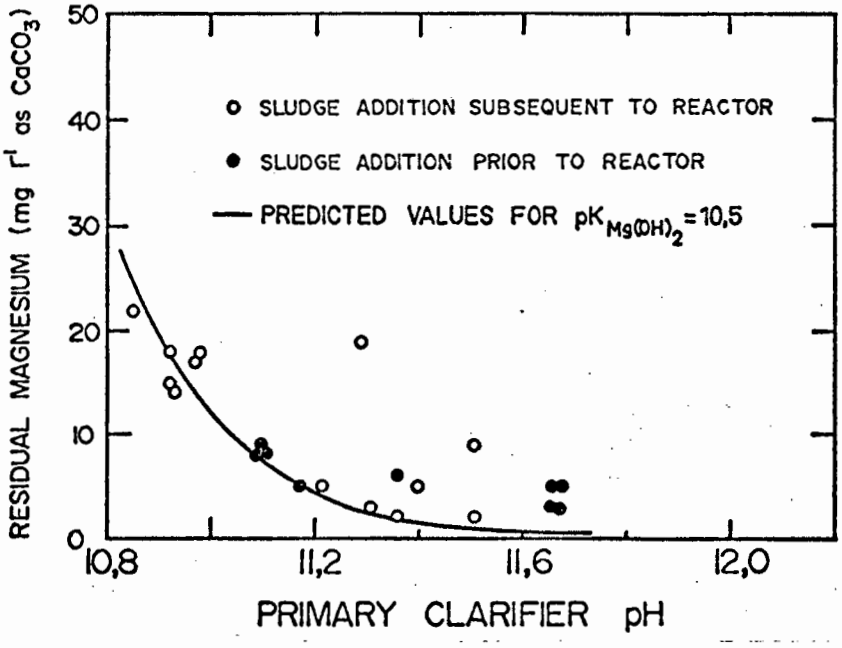


Figure 5.16. Primary clarifier residual magnesium concentration as a function of pH for long retention time and sludge age

5. REACTION WITH CARBON DIOXIDE FROM THE AIR

One of the potential problems associated with lime treatment is the reaction of lime with atmosphereic carbon dioxide. Two aspects of this problem are,

(1) the reactions of lime slurries with CO_2, and
(2) the reaction of alkaline lime-treated secondary effluent with CO_2.

5.1 Lime Slurry - CO_2 Reaction

In the literature little attention appears to have been given to absorption of CO_2 by lime slurries in holding tanks under the highly alkaline conditions prevailing in such systems, although reaction with atmospheric carbon dioxide appears a distinct possibility. If this takes place to any significant degree, active lime will be lost and the fraction of insolubles in the sludge will increase. On the Stander Plant no obvious adverse effects have been noted, but the effects may not be readily apparent.

To investigate the absorption of carbon dioxide by lime slurry, 2 litres of a 5 percent lime slurry was made up in a 2½ ℓ plastic beaker, using commercial grade lime and secondary effluent. The slurry was stirred vigorously using a magnetic stirring bar. The stirring was such that a vortex drew air continuously into the slurry. Slurry samples (25 mℓs) were withdrawn from the reaction mixture at 0, 10, 30, 60, 120, 150 and 180 minute intervals and analysed for active lime, using the sugar method (SABS, 1955).

Experimental results for the reaction of lime slurry with atmospheric carbon dioxide are listed in Table 5.8. It is evident from these results that even at long batch reaction times vigorous stirring in the presence of atmospheric carbon dioxide results in a minimal decrease in the slurry active lime content (0,3 - 2,0 percent). The reaction of atmospheric carbon dioxide with lime slurries, under conditions prevailing on the full-scale plant, i.e. vigorous stirring in a slurry for 10-30 minutes mean residence time, therefore does not appear to present any problems. As a precaution slurry holding tanks could be placed under cover to minimize the free movement of air in contact with the lime slurry.

Table 5.8

Changes in lime slurry active lime concentration as a function of contact time with the atmosphere

Batch Reaction Time	Active Lime
Minutes	g ℓ^{-1} (as CaO)
0	27,9
10	27,4
30	27,5
60	27,7
90	27,7
120	27,3
150	27,3
180	27,8

5.2 Alkaline Effluent - CO_2 Reaction

Experience with the lime treatment process on the Stander Plant has provided clear evidence of the severe problems of post clarifier calcium carbonate precipitation and scale formation in clarifier troughs, pipelines and pumps. The causes of this problem may be two-fold,

(1) Slow secondary calcium carbonate precipitation. The clarifier effluent may be slightly supersaturated due to incomplete precipitation in the precipitation zone of the clarifier and result in post clarifier precipitation.

(2) Absorption of CO_2 from the air by the highly alkaline lime-treated effluent. This phenomenon is clearly evident at the clarifier surface, since at the effluent-air interface a thin "skin" of $CaCO_3$ is often evident. Since this effect is observed at the clarifier surface, where there is little surface renewal, CO_2 absorption must be even more pronounced at the overflow weir where effluent and air mix under turbulent conditions, due to free flow of the effluent over the weir.

In the lime treatment process the sole reason for demanding a stable effluent from the sludge blanket clarifier is to minimize post precipitation problems, in particular epitaxial growth of $CaCO_3$ on the pipe surfaces in contact with the treated effluent. Considerable effort is expended to ensure stability by developing specific reactor-clarifier configurations with sludge recirculation. It seems, therefore, incongruous to nullify these efforts by reintroducing supersaturated conditions in a stable effluent by allowing carbon dioxide absorption from the air.

The stable effluent produced in the clarifier contains virtually no suspended $CaCO_3$ particles and hence the production of supersaturated conditions by CO_2 absorption from the air will lead to long induction periods internal to the liquid mass. However, if a crystal surface is available in the pipes, in the form of scale on the pipe walls, it will favour growth on the wall from the supersaturated solution.

Measurement of the total acidity concentrations before and after the clarifier overflow weir gave inconclusive evidence of CO_2 absorption. This is not unexpected as the quantity of CO_2 absorbed is small. The scale formation cannot be attributed to incomplete precipitation in the clarifier - the absence of extensive precipitation on the surfaces of the clarifier in the clear liquid zone, in contrast to the extensive scale growth on the overflow weir, collecting trough and pipes transporting the treated effluent, indicate that it is the CO_2 absorption which results in the long-term scaling effects.

Two possible practical solutions to this problem are :

(a) Preventive measures must be taken to minimize carbon dioxide uptake from the air. This could be achieved by covering clarifier overflow weirs and collection troughs, to exclude free movement of air. Design ideas regarding this aspect are presented in Chapter 7.

(b) Accepting scale formation as a result of CO_2 absorption from the air and using open ducts (where possible) instead of pipes, to facilitate easy removal of scale. However, it is unlikely that precipitation will proceed to equilibrium in open ducts so that there may still be problems of post precipitation in pumps. Hence, where possible pumps should be replaced by gravity flow systems.

5.3 Conclusions

(1) The reaction of lime slurries with atmospheric carbon dioxide, under normal slurry make-up and distribution conditions, has a minimal effect on reducing the active lime content of the lime slurry.

(2) Significant long-term scaling problems are induced by the small quantities of CO_2 absorbed in the overflow and at the surface of the clarifier. To minimize CO_2 absorption clarifier weirs and troughs should be suitably covered or open ducts and gravity flow systems should be used instead of pipes and pumps.

6. GENERAL CONCLUSIONS

(1) The most effective mode of lime treatment on the full-scale Stander Plant was a reactor-clarifier combination with sludge recirculation to a point prior to the reactor. This mode of operation resulted in the lowest residual calcium and magnesium concentrations in the clarifier effluent. The beneficial effect of the point of sludge discharge prior to the reactor and the maintenance of a sludge blanket clarifier is mainly to be noted in magnesium removal. Magnesium precipitation to "equilibrium" appears to be the deciding factor in the choice of residence times and sludge age.

(2) The Ca_T^{2+} versus pH and Mg_T^{2+} versus pH relationships for clarifier effluent, obtained during operation of the optimal treatment mode in the pH range 10,8 to 11,4, are adequately predicted by using a Modified Caldwell-Lawrence Diagram with $pK_{CaCO_3} = 6,7$ and $pK_{Mg(OH)_2} = 10,5$.

(3) Increasing the lime reactor and sludge blanket clarifier residence times and sludge age by a factor of two did not result in any significantly increased calcium or magnesium removal, as compared to removals at normal residence times and sludge ages, i.e. reactor and clarifier residence times of 10,8 and 66 minutes, respectively, and sludge ages of about 3 to 5 days. These standard conditions appeared to be sufficient to give an effluent

stable with respect to Ca_T^{2+} and Mg_T^{2+}.

(4) An air-sparging mixing system in the full-scale lime reactor resulted in significant effluent CO_2 absorption with associated ineffective use of lime and increased sludge production. Mechanical stirring is recommended.

(5) Small quantities of CO_2 absorbed by the effluent at the clarifier surface, overflow weir and the collection trough cause significant long-term scaling problems at clarifier weirs, troughs and pipes transporting treated effluent. It was suggested that clarifier weirs and troughs be covered suitably to minimize CO_2 absorption opportunity. If restriction of the free movement of air in contact with alkaline effluent is not possible, open ducts and gravity flow systems should be used instead of pipes and pumps.

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CHAPTER 6

$CaCO_3$ and $Mg(OH)_2$ ACTIVITY PRODUCT CONSTANTS

1. INTRODUCTION

From a practical point of view plots of the residual dissolved calcium and magnesium versus pH (see Chapter 5, Figures 5.11 and 5.12) are adequate to characterize a particular lime-treated effluent. These plots may form a basis for the design of pilot or full-scale plant. For the purpose of identifying general tendencies and eventually establishing generalized methods for the characterization of waste waters with fewer tests, say for example knowing the initial constitution of the water only, a model describing the behaviour of lime-treated effluents is required.

In Chapter 4 the Modified Caldwell-Lawrence Diagram was accepted as a model for characterizing lime-treated effluents. A fit of the model predictions with the experimental data was obtained by a trial and error selection of pK_{CaCO_3} and $pK_{Mg(OH)_2}$ values. The pK values obtained in this way are empirical. The fact that reasonable correlation between predicted and experimental results could be obtained indicates that perhaps these pK values are real constants reflecting the influence of contaminants on the thermodynamic constants. In the literature review (Chapter 2, Section 4) it was shown that the thermodynamic solubility product constants are very sensitive to the presence of phosphorous and organic materials. If the solubility products of $CaCO_3$ and $Mg(OH)_2$ precipitated in lime-treated effluents should show values near those selected to give good predictions in the Modified Caldwell-Lawrence Diagram, a scientific basis for the use of the Diagram for lime-treated effluents will have been established.

In order to determine solubility products for any particular system the precipitates of that system must be defined and precipitation must proceed to equilibrium. Neither of these conditions are met in lime-treated effluent systems. The precipitates are thought to be $CaCO_3$, $Mg(OH)_2$ and $Ca_3(PO_4)_2$. The exact crystallographic forms are not known, with the exception of calcite. However, even in the case of calcite other minerals may be incorporated in the calcite crystals which may change the calcite solubility product value. The attainment of equilibrium is also in doubt, since to attain true equilibrium may take very long periods. Even if solubility products are determined for long reaction periods, the problem may still not be resolved as a result of the establishment of equilibria other than those applicable to the process, due to slow solid-solid reactions.

It is clear from the above that the problem of predicting the chemical constitution of lime-treated effluents is not a true equilibrium problem, but rather one of predicting near equilibrium states. Fortunately, if appropriate conditions are applied such as high seed crystal mass, apparently stable effluents can be produced within reasonably short reaction periods, say 1-5 minutes. For these effluents the concentrations of ionic species at "near equilibrium" may be characterized by the activity products of the hypothesized precipitants. Because these activity products do not appear to change significantly over the time periods of interest to the lime process, they are referred to as "activity product constants".

The purpose of this investigation was to establish the activity product constants (APC) of $CaCO_3$ and $Mg(OH)_2$ precipitated from secondary effluent in the lime treatment process. As the exact constitution of the precipitants is not known, the values of the APCs based on $CaCO_3$ and $Mg(OH)_2$ may show variation under different operating conditions. It was intended to identify the principal factors apparently affecting these APC values. This aspect of necessity is empirical, for if the forms of the precipitants are incorrectly

assumed the APC values inevitably will show variation, but the factors that apparently cause the variations may be quite fictitious. For example both Merrill (1974) and Wiechers (1976) reported data which shows that the $Mg(OH)_2$ activity product for lime-treated raw sewage is apparently strongly pH dependent. Merrill (1974) formulates this dependency as follows,

$$p[APC(Mg(OH)_2)] = 25,537 - 1,382.pH \quad .... \quad (6.1)$$

It is patently impossible that the activity product constant should be a function of pH, for indirectly the magnesium hydroxide APC incorporates pH, making the APC value a function of itself. The variation probably arises due to the $Mg(OH)_2$ precipitation not being complete, or, $Mg(OH)_2$ is not the physical form in which magnesium is being removed from solution, or, some other unknown effect.

2. GENERAL METHODS

A treated effluent at "near equilibrium" was prepared as follows : A sample of the precipitation reactor contents was sealed in an air-tight glass container and shaken mechanically for 24 hours or longer. After this relatively long batch reaction period the sample was vacuum filtered (Whatman No. 542) to remove suspended solids. Subsequently temperature, pH and Alkalinity were determined immediately on a portion of the filtrate. The remaining portion was acidified to pH 4 with 0,1N H_2SO_4 (to prevent ammonia loss from samples with high pH values) and analysed for Ca, Mg, NH_3-N, PO_4-P, COD, Na, K, Cl, NO_3 and SO_4, where applicable.

From the above determined values for total dissolved Ca, Mg, NH_3-N, PO_4-P, Na, K, Cl, NO_3 and SO_4 as well as pH, Alkalinity and temperature, it is possible to calculate the ionic strength, free ion concentrations and activities of Ca^{2+}, CO_3^{2-}, Mg^{2+} and OH^- using computer programme WATEQ 1. This programme is an updated version of programme WATEQ published by Truesdell and Jones (1973). It

includes ion pairing effects for all the inorganic species analysed in the filtered sample. Using free ion activities the $CaCO_3$ and $Mg(OH)_2$ activity products (AP) were calculated from,

$$AP(CaCO_3) = (Ca^{2+})(CO^{2-}_3) \quad .... \quad (6.2)$$

$$AP(Mg(OH)_2) = (Mg^{2+})(OH^-)^2 \quad .... \quad (6.3)$$

Activity product determinations were conducted for both laboratory and full-scale test samples, for both $CaCO_3$ and $Mg(OH)_2$. Each set of tests will be described separately in the following sections. A wide variety of experimental conditions were studied to observe the effects of different conditions on the activity product values, i.e. effluents of widely varying quality, degree of treatment (lime treatment and recarbonation) and temperature.

Once the experimental AP-values were available, the influence of parameters such as temperature, pH, PO_4-P, Mg, COD, NH_3-N and stabilization time were investigated. This was done as follows : A hypothesis was made that a basic relationship exists between the APC-value and a specific parameter, for example the standard relationship for modelling the effect of temperature on equilibrium constants is (Truesdell and Jones, 1973),

$$pK = A + B.T + C/T \quad .... \quad (6.4)$$

where T = the absolute temperature (^oK)
A,B,C = model constants

This model was then tested by means of a computer programme, NLIN (Middleton, 1968). Using paired sets of p(AP) and T as input data, the programme calculates the values of A, B and C to give the best fit to p(AP) and T values by means of a non-linear least squares regression analysis.

In addition to the temperature effect, which was always assumed to be of the form given by Eq. (6.4), the effect of another parameter, say X, such as pH, PO_4-P, Mg, COD or NH_3-N, was incorporated in the model as follows,

$$p(APC) = A + B.T + C/T + D.X \quad .... \quad (6.5)$$

A similar procedure to the one described above was again followed to determine the best fit values for A, B, C and D. The standard error (S.E.) in the fit was defined as,

$$S.E. = \left\{\frac{\text{sum of the squares of residuals}}{\text{degree of freedom}}\right\}^{\frac{1}{2}} \quad .... \quad (6.6)$$

$$= \frac{\{\Sigma(\text{Obs.} - \text{Pred.})^2\}^{\frac{1}{2}}}{N - K} \quad .... \quad (6.7)$$

where Obs. = observed p(APC) values
Pred. = Predicted p(APC) values
N = number of observed values
K = number of model coefficients

A reduction of greater than 10 percent in the standard error was taken to indicate that the parameter X had a significant effect and it was retained in the model. If a reduction of less than 10 percent was effected by incorporating X into the model, it was taken that X had no significant effect and was not retained.

3. PURE SYSTEMS

A pure system is defined as a synthetic system consisting of deionized water containing only analytical reagent grade purity dissolved salts. For instance, in the case of a pure calcium carbonate system, $CaCl_2$, NaOH and $NaHCO_3$ may be used. In the case of a pure magnesium hydroxide system, $MgCl_2$ and NaOH may be used.

Pure system studies of calcite solubility and solubility products have been dealt with exhaustively in the literature, as reported in Chapter 2, Section 2.2. A few pure system studies of magnesium hydroxide solubility and solubility products have been reported in the literature, and are also reviewed in Chapter 2, Section 2.3. Loewenthal and Marais (1976) have tested the validity of literature reported values of calcium carbonate solubility products for synthetic solutions simulating practical softening process conditions. Their predictions, using the Modified Caldwell-Lawrence Diagram, were in good agreement with their experimental results.

In this investigation a few confirmatory tests were made to establish if synthetic solutions simulating lime-treated effluent displayed activity product values identical to corresponding calcite solubility product values.

3.1 Experimental Investigation

During pure synthetic calcium carbonate precipitation tests on the laboratory bench-scale plant (Chapter 3, Section 4) duplicate 1ℓ reactor effluent samples were taken in a few of the tests. Calcite ($\pm$ 10 g ℓ^{-1}) was added to one of each of the duplicate sets of samples. The samples were placed in air-tight bottles and shaken mechanically for 24 to 48 hours. Sample analysis and data reduction procedures are described in Section 2. Raw data collected in this test series are listed in Appendix 6.

Experimentally determined calcium carbonate activity products as a function of pH are shown in Figure 6.1. The $CaCO_3$ activity products for solutions with high concentrations of calcite seed crystals in the pH range 8,0 to 9,5 are in excellent agreement with $CaCO_3$ solubility products predicted from thermodynamic considerations by Truesdell and Jones (1973), i.e. $K_{CaCO_3} = 10^{-8,35}$ (see Chapter 2, Section 2.2). At pH values greater than 9,5 the agreement is somewhat less good. The $CaCO_3$ activity products for solutions without any added $CaCO_3$ seed crystals were significantly lower than the thermodynamic $CaCO_3$ solubility product, i.e. $10^{-7,70}$ to $10^{-8,06}$ as compared to $10^{-8,35}$ (see Figure 6.1). This indicates that in the absence of calcite seed crystals true thermodynamic equilibrium is not attained under conditions simulating the lime treatment process, even at reaction times of 48 hours.

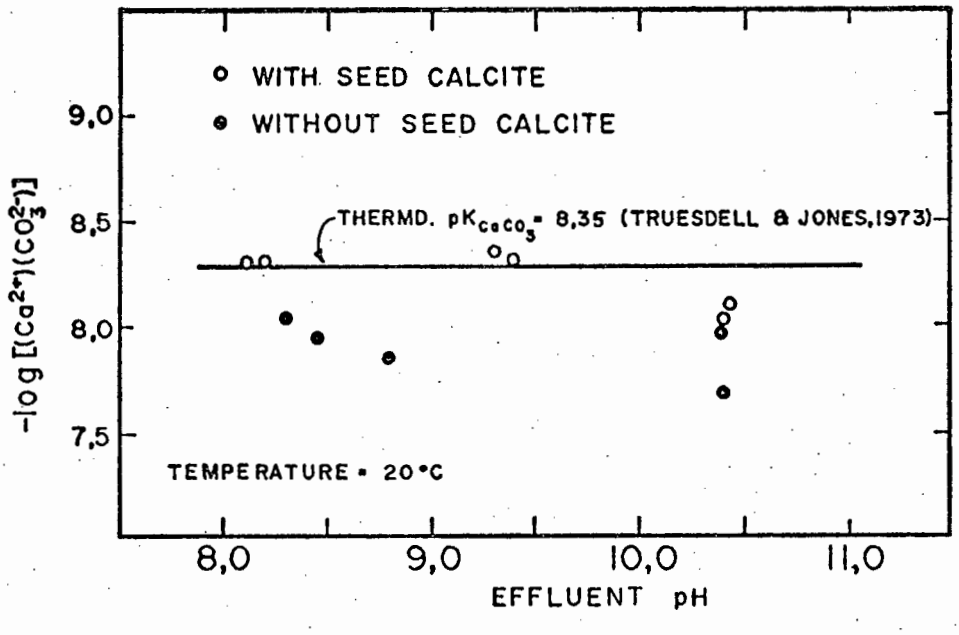

Figure 6.1. $CaCO_3$ activity product values for pure synthetic solutions (in the absence of magnesium ions)

4. BENCH - SCALE PLANT STUDIES

Calcium carbonate and magnesium hydroxide activity product values for lime-treated waste water reported in the literature (Chapter 2, Section 5.2) and also determined in the full-scale plant studies (see next Section), are up to two orders of magnitude larger than the thermodynamic solubility product values of calcite and brucite. It is not clear if this discrepancy is due to the heterogeneous nature of lime-treated effluent, or, insufficient surface area for crystal growth. Studies reported in Chapter 4, Section 4 indicate that in the absence of seeding sludge, the ionic species residual concentrations (and hence activity products) decrease when the reaction period is increased from 14 minutes to 24 hours. It was also demonstrated that seed sludge inoculation has an effect similar to the lengthening of retention times, i.e. it decreases residual calcium, magnesium, and alkalinity concentrations. However, these tests do not necessarily reflect equilibrium conditions.

To establish if the apparent difference between the $CaCO_3$ activity product values for lime-treated secondary effluent and the thermodynamic solubility product constant for calcite was due to insufficient surface for crystal growth or insufficient time for attaining equilibrium, a study was made where effluent samples were inoculated with high concentrations of pure calcite and very long equilibration periods were allowed.

Duplicate 1ℓ samples of CSTR effluent were collected during laboratory bench-scale plant runs with secondary effluent (see Chapter 4, Section 4). The samples were taken from the plant when the CSTR was operated at a residence time of 14 minutes. Effluent pH values were in the range 10,0 to 11,4. Analytical reagent grade calcite (app. 10000 mg ℓ^{-1}) was added to one sample of each of the duplicate sets of samples. The samples were shaken mechanically for at least 24 hours and up to 240 hours in a constant temperature room at 20°C. Procedures for sample analysis and data reduction are described in Section 2. Raw data collected during the investigation are listed in Appendix 11.

4.1 Results and Discussion

Typical results for experimentally determined p[AP($CaCO_3$)] values, i.e. the negative logarithm of the calcium carbonate activity product, are listed in Table 6.1 and are graphically illustrated in Figure 6.2.

Table 6.1

Effect of equilibration period and pure calcite inoculation on p[AP($CaCO_3$)] values for lime-treated secondary effluent (laboratory tests)

CSTR REACTION pH	BATCH EQUILIBRATION TIME	p[AP($CaCO_3$)] Without / With calcite	
-	hours	-	-
10,0	24	6,72	7,10
	120	6,83	7,03
10,5	48	6,77	7,18
	144	6,88	7,30
11,0	24	6,86	7,06
	134	6,99	7,04
11,2	72	6,89	7,15
	240	7,00	7,19
11,4	192	6,83	6,91

The p[AP($CaCO_3$)] values listed in Table 6.1 confirm that changes in this parameter still take place even at reaction periods of 24 hours, both in the absence and presence of inoculated pure calcite. It may therefore be concluded that true equilibrium for the calcium carbonate precipitation reactions in lime-treated secondary effluent is not established within 24 hours. However, the changes in the p[AP($CaCO_3$)] values at reaction periods longer than 24 hours are so small that for practical purposes the 24 hour activity products may be considered as *constants*.

The experimental results illustrated in Figure 6.2 indicate the effect inoculation of pure calcite had on the p[AP($CaCO_3$)] values, i.e. the average p[AP($CaCO_3$)] value increased from 6,88 to 7,14, which is still considerably lower than the thermodynamic pK_{CaCO_3} value of 8,35. Therefore, irrespective of the contact with high concentrations of pure calcite or long reaction periods, the calcium carbonate activity product value for lime-treated secondary effluent remained approximately one order of magnitude greater than the thermodynamic $CaCO_3$ solubility product.

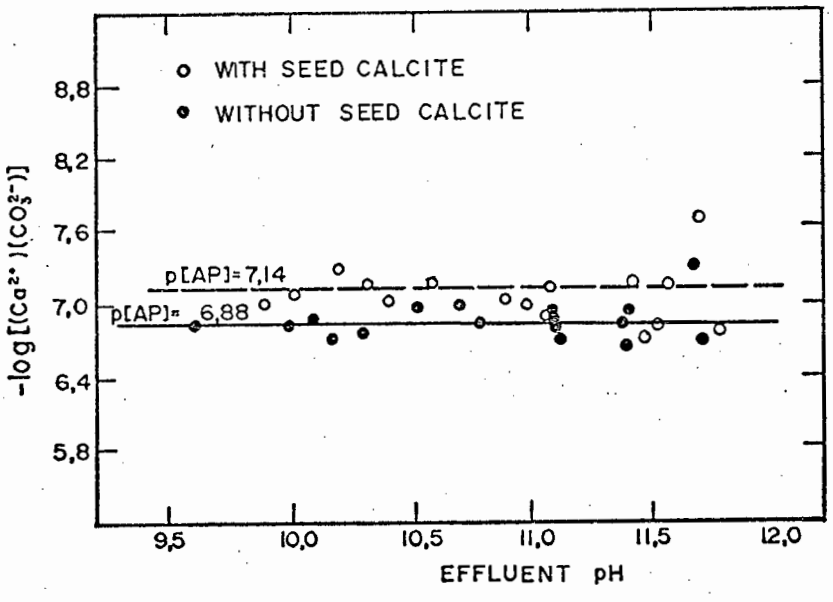

Figure 6.2. $CaCO_3$ activity product values for lime-treated secondary effluent, with and without calcite seed (laboratory tests)

The $p[AP(CaCO_3)]$ values are plotted as a function of pH in Figure 6.2. The values appear independent of pH although there is some random fluctuation about the average value. The average values for the two systems are 6,88 in the absence of pure calcite crystals and 7,14 in the presence of calcite crystals. The observation that $p[AP(CaCO_3)]$ is independent of pH is consistent with similar observations by Seiden and Patel (1969) and Merrill* (1974), who reported $p[AP(CaCO_3)]$ values of 5,9 and 6,5 for lime-treated secondary effluent and lime-treated raw sewage, respectively.

Typical results for experimentally determined $p[AP(Mg(OH)_2)]$ values, i.e. the negative logarithm of the magnesium hydroxide activity product, are shown in Figure 6.3. The $p[AP(Mg(OH)_2)]$ values varied randomly over the pH range studied. The magnitude of the variations was significant, i.e. from 10,62 to 12,28. Two reasons for this variability were apparent,

(1) After 24 hours or longer reaction periods the residual magnesium concentration of effluents with pH values higher than 11,0 were very low, i.e. less than 0,5 mg ℓ^{-1} (as Mg). These low concentrations were of the same order of magnitude as the accuracy of the analytical method used for determining the magnesium concentrations (atomic absorption). The analytical accuracy of reported residual magnesium concentrations for effluents with pH values higher than 11,0 was therefore poor. Derived $p[AP(Mg(OH)_2)]$ values based on these magnesium concentrations in consequence were also unreliable.

*Merrill (1974) indicated very slight pH dependence, i.e. $p[AP(CaCO_3)]$ = 6,47 and 6,46 at pH values 10,0 and 11,0, respectively. This pH dependence is so small that it may be neglected for all practical purposes.

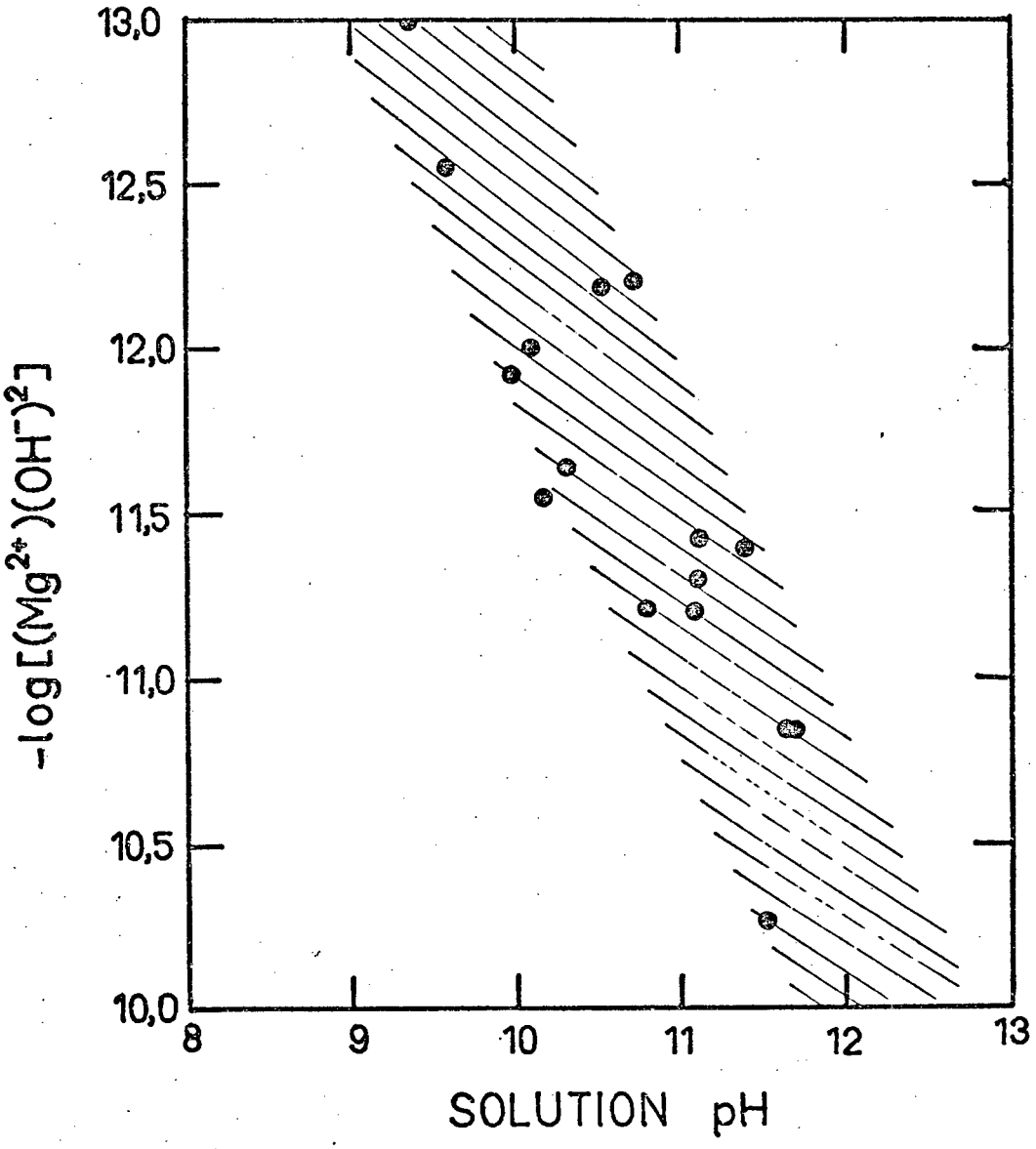

Figure 6.3. Plot indicating scatter in laboratory test determined $p([Mg^{2+}][OH^-]^2)$ values

(2) At pH values lower than 10,5 the controlling mechanism of magnesium removal is not necessarily magnesium hydroxide precipitation, i.e. magnesium ions may be precipitated as magnesian calcite and magnesium silicate or may be adsorbed onto calcite particles. Therefore, the experimentally determined $p[AP(Mg(OH)_2)]$ values in this pH range do not necessarily correspond to the residual values resulting from $Mg(OH)_2$ precipitation.

For these reasons in this set of experiments no firm conclusion related to magnesium hydroxide precipitation could be attached to the $p[AP(Mg(OH)_2)]$ values determined.

In order to increase the scope of the investigation, activity product values for $CaCO_3$ and $Mg(OH)_2$ were determined for effluents from the full-scale plant precipitation reactors under a variety of experimental conditions.

5. FULL-SCALE PLANT STUDIES

Calcium carbonate and magnesium hydroxide activity product values were determined for effluent samples from the lime and recarbonation reactors of the full-scale Stander Plant. A number of different plant conditions were selected for this study to ascertain the effects of influent quality, lime dosage, carbon dioxide dosage and temperature on the resultant $CaCO_3$ and $Mg(OH)_2$ activity product values.

5.1 Lime-treated Secondary Effluent

Samples of lime-treated secondary effluent were drawn from the effluent stream from the full-scale plant reactor. The lime dosage rate was systematically changed to effect pH values in the range 10,0 to 11,6 in the reactor. Sludge was not recirculated to the reactor during these tests. Effluent samples were shaken mechanically at ambient temperatures in the range 8 to 23°C. Sample analysis and data reduction procedures are described in Section 2. Raw data collected during this investigation are listed in Appendix 12.

$CaCO_3$ activity product

Typical $CaCO_3$ activity product values for lime-treated secondary effluent are listed in Table 6.2. Fitting Eq. (6.4) to 70 paired data sets for $p[APC(CaCO_3)]$ and T, resulted in the following model,

$$p[APC(CaCO_3)] = 25,237 - 0,0291.T_k - 2910,22/T_k \quad .... \quad (6.8)$$

where T_k = the absolute temperature (^oK)

Table 6.2

Typical calcium carbonate activity product values for lime-treated secondary effluents (full-scale tests - no sludge recirculation)

Total Dissolved Calcium*	Total Alkalinity*	pH*	Temperature*	$p[APC(CaCO_3)]$	
mg/ℓ (as Ca)	mg/ℓ as $CaCO_3$		^oC	Experimental	Predicted*
46	120	10,91	22,0	6,778	6,775
51	112	10,45	22,3	6,702	6,776
55	129	11,20	23,0	6,947	6,779
48	102	10,95	19,0	6,821	6,761
52	85	10,72	20,5	6,813	6,768
86	160	11,42	13,6	6,726	6,766
49	82	10,86	13,6	6,819	6,731
51	113	10,72	12,0	6,702	6,720
64	137	10,95	16,5	6,585	6,748
65	125	10,62	18,0	6,591	6,756

*Parameters measured in filtered 24 hour stabilized lime-treated secondary effluent; Predictions based on Eq. (6.8).

Incorporating pH, COD, Mg, PO_4-P and NH_3-N in Eq. (6.6), as set out in Eq. (6.5), indicated that not one of these parameters had any significant effect on $p[APC(CaCO_3)]$.

The predicted effect of temperature on $p[APC(CaCO_3)]$, as given by Eq. (6.8), gives an increase of 0,05 for an increase of ten degrees Celsius which is of the same order of magnitude as predictions by Truesdell and Jones (1973) based on thermodynamic considerations, i.e. 0,08 per 10^oC. The temperature effect may be considered negligible for all practical purposes.

The average $p[APC(CaCO_3)]$ value for lime-treated secondary effluent is approximately 1,5 p[APC] units smaller than the thermodynamic pK_{CaCO_3} value for calcite, i.e. 6,8 as compared to 8,3 (see Figure 6.4). Within the limits of this study pH and temperature had no significant effect on the $p[APC(CaCO_3)]$ value. Variations in influent and treated-effluent concentrations of ortho-phosphate, magnesium, COD and ammonia also appeared to have no direct effect on the $p[APC(CaCO_3)]$ value. The question thus remains, what is the reason for the large difference between the $CaCO_3$ activity product values for lime-treated secondary effluent and the thermodynamic solubility product for calcite?

The pure system investigation indicated that equilibrium with respect to calcite is only attained in pure synthetic calcium carbonate solutions under conditions of high calcite seed mass and 24 hours (or longer) equilibration periods. In heterogeneous systems equilibrium with respect to calcite could not be established, even for reaction times of 240 hours and reaction in the presence of high concentrations of pure calcite. Strictly speaking therefore, the activity product values for heterogeneous sytems reported in this investigation are not solubility products, but rather transient activity products. However, since changes in the experimentally determined activity products were very small after equilibration periods of 24 hours, or longer, these activity products can for all practical purposes be considered as constants. Thus it may be concluded

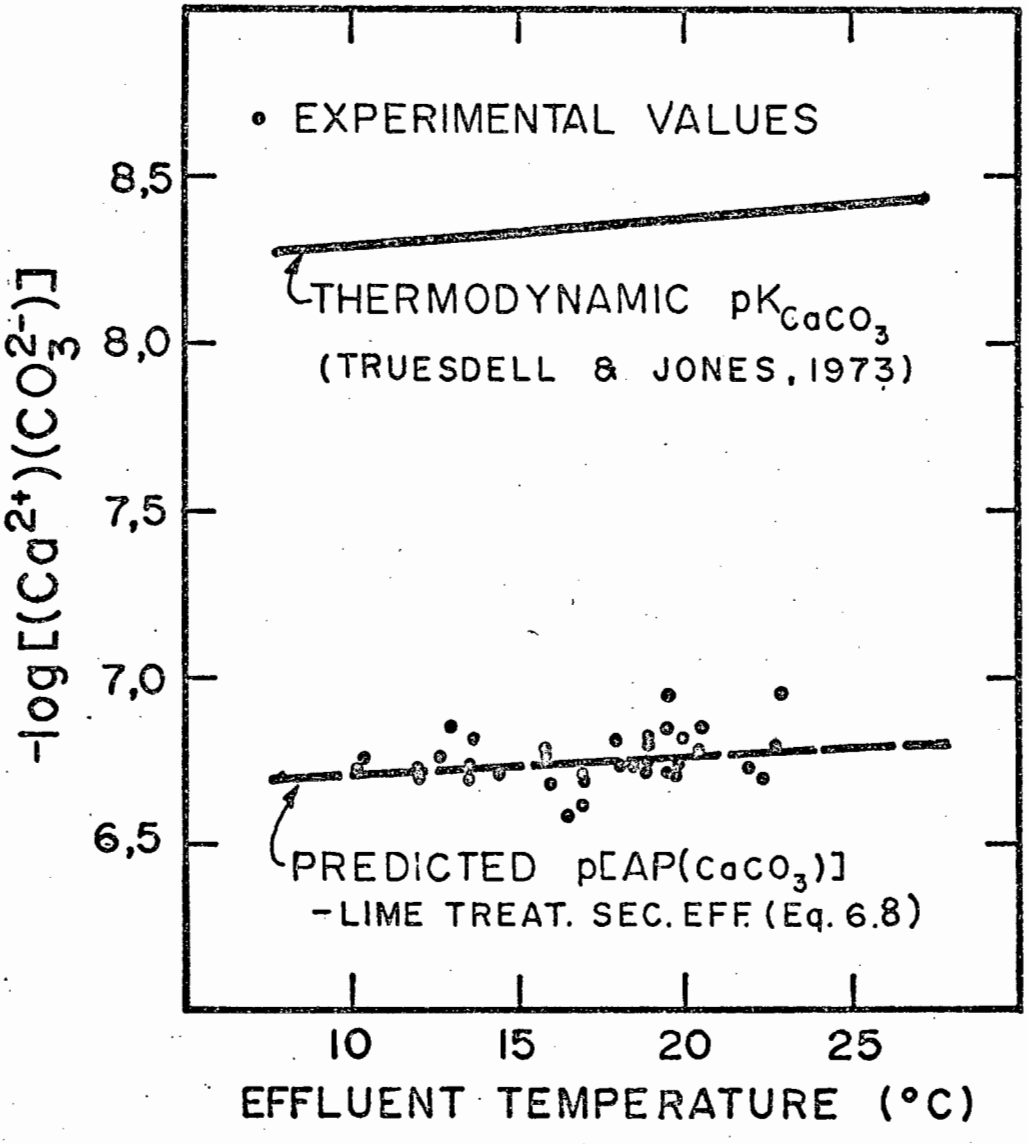

Figure 6.4. Experimental and predicted calcium carbonate activity product values for lime-treated secondary effluent (full-scale test - no sludge recirculation) and predicted values for calcite only

that one of the reasons for the experimentally determined calcium carbonate activity product constants for heterogeneous effluents being considerably larger than the calcite solubility product, is inhibited precipitation kinetics.

Several other, or additional, hypotheses have been proposed in the literature. Larson, Sollo and McGurk (1973) and Doner and Pratt (1969) attributed apparent increases in calcium carbonate solubility for heterogeneous systems to the formation of ion pair complexes of calcium with bicarbonate, carbonate, hydroxide and sulphate ions, i.e. $CaHCO_3^+$, $CaCO_3^o$, $CaOH^+$ and $CaSO_4^o$. However, these ion pair complexes were taken into consideration in the calculation of free Ca^{2+} and CO_3^{2-} concentrations in this study, thus eliminating or reducing the value of this hypothesis as an explanation of the phenomenon of apparently increased $CaCO_3$ solubility.

The hypothesis that the dissolved organic matter in treated effluents could complex a significant fraction of the free Ca^{2+} ions was considered. However, the range of dissolved COD concentration of lime-treated secondary effluent is very low in comparison to the range of dissolved calcium concentration, i.e. 15 to 24 mg ℓ^{-1} (as O) as compared to 100 to 250 mg ℓ^{-1} (as $CaCO_3$), respectively. Therefore, even if all the organic matter could complex with calcium on a 1:1 basis, which is very unlikely, this would still not explain the marked increased solubility for calcium carbonate in lime-treated effluents

The important role which phosphates play in effecting the solubility of calcium carbonate has been discussed in Chapter 2 (Section 4.1). Reddy and Nancollas (1973) reported on the severe inhibition of calcium carbonate crystallization by very low concentrations of phosphates and polyphosphates and Capri and Marais (1975) on the effects of ortho-phosphates. Inhibition was attributed to phosphate adsorption onto crystal growth sites. From the work of Capri and Marais (1975) it is also evident that ortho-phosphate is incorporated in the calcium carbonate crystal lattice. This will result in changes in

the surface characteristics of the crystal and hence the rate of $CaCO_3$ precipitation and its solubility.

Lime-treated secondary effluents and recarbonated effluents contain phosphates (organo- and ortho-phosphate) in low concentrations (<1,0 mg ℓ^{-1} as P). Deviations from predicted thermodynamic pK_{CaCO_3} values for these effluents could possibly be due to the inhibiting effect of these phosphates. If this hypothesis is correct, the increase in apparent solubility product values (activity product constants) should, to some extent, depend on the concentration of the phosphates in the system. Evidence in favour of this hypothesis has been reported by Merrill and Jorden (1974). They found the experimentally determined $CaCO_3$ activity product constants to be roughly proportional to system waste strength and therefore, by implication, the phosphate concentration (Table 6.3). It is noteworthy that for secondary effluent the pK_{CaCO_3} value reported by Merrill and Jorden and in this study (Chapter 4), are identical, i.e. 6,7.

$Mg(OH)_2$ activity product

Typical experimentally determined magnesium hydroxide activity product values obtained on the full-scale plant are listed in Table 6.4. The standard equilibrium constant-temperature relationship, Eq. (6.4), was fitted to paired sets of the experimentally determined $p[AP(Mg(OH)_2)]$ and T values, using the computer programme, NLIN (Middleton, 1968).

Table 6.3

$CaCO_3$ activity product constants for four different types of lime-treated effluent (After MERRILL and JORDEN, 1974)

Effluent Type	$p[APC(CaCO_3)]$
Well water	7,4
Primary and Secondary effluent	6,7
Raw waste	6,4
Anaerobic digester supernatant	6,3

Table 6.4

Typical magnesium hydroxide activity product values for lime-treated secondary effluent (full-scale tests - no sludge recirculation)

Total Dissolved Magnesium *	pH *	Temperature *	p[APC($Mg(OH)_2$)]	
			Experimental	Predicted **
mg ℓ^{-1} as Mg	-	°C	-	-
12	10,50	12,0	11,544	11,742
6	10,86	18,6	10,670	10,866
8	10,73	18,3	10,834	11,069
3	11,42	20,0	9,822	9,991
9	10,90	17,0	10,550	10,889
2	10,97	22,0	10,735	10,549
2	10,86	13,6	11,461	11,130
9	10,90	17,0	10,550	10,889
5	10,72	18,3	11,010	11,084
3	10,69	13,5	11,651	11,381

*Parameters measured in filtered 24 hour stabilized lime-treated secondary effluent; **Predictions based on Eq. (6.9).

The standard error in fitted p[AP($Mg(OH)_2$)] values was 0,346. An attempt was made to improve this fit by including a term in the model for the major parameters characterising the secondary effluent and the lime-treated effluent, as in Eq. (6.5). Of these only the pH of the lime-treated effluent could be correlated with p[AP($Mg(OH)_2$)] values to give,

$$p[AP(Mg(OH)_2)] = -82,464 + 0,162.T_k + 17988,7/T_k - 1,443.pH \quad .... \quad (6.9)$$

The above relationship was obtained from a fit to 28 data points (only data sets with Mg>2mg ℓ^{-1}(as Mg) and pH>10,5 were used, to overcome objections raised in Section 4.2). The standard error in fitted $p[AP(Mg(OH)_2)]$ values is 0,207, which is of the same order of magnitude as the experimental error, i.e. 0,210. The data scatter about the fitted p[AP] values is 2,05 percent (see Figure 6.5).

The modelled effect of pH on $p[AP(Mg(OH)_2)]$ values is significant, i.e. a 0,1 unit increase in pH corresponded to a 0,14 unit decrease in $p[AP(Mg(OH)_2)]$. A significant pH dependence of the magnesium hydroxide activity product constant was also noted by Merrill (1974) for lime-treated raw sewage (see Chapter 2, Section 5.2). He reported the following relationship,

$$p[AP(Mg(OH)_2)] = 25,537 - 1,382.pH \quad \ldots\ (6.10)$$

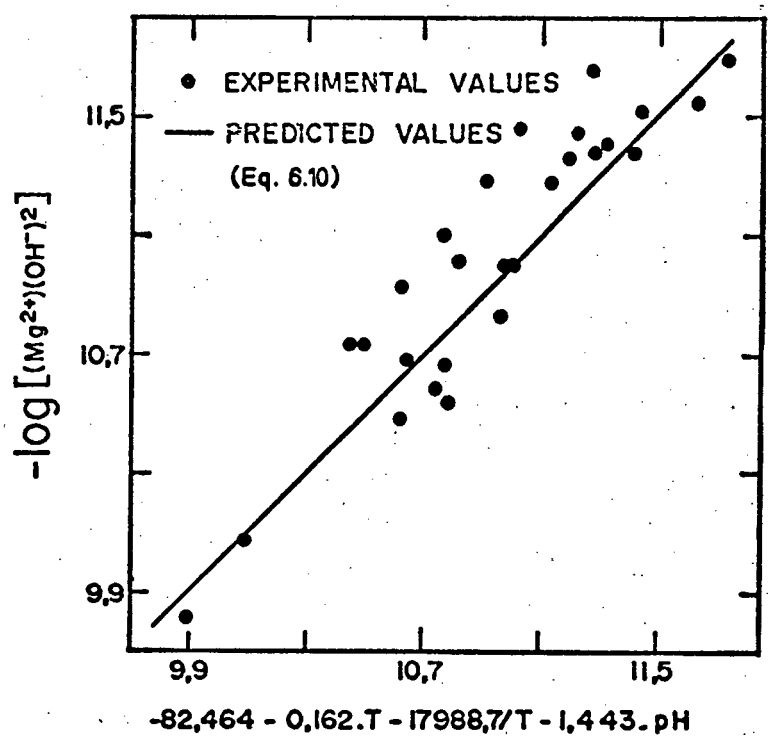

Figure 6.5. Experimental and predicted $Mg(OH)_2$ activity product values for lime-treated secondary effluent (full-scale test - no sludge recirculation)

Both sets of tests were conducted in the absence of recirculated sludge which may have resulted in insufficient driving force for establishing equilibrium for the slow $Mg(OH)_2$ precipitation reaction (Liu and Nancollas, 1973). Residual magnesium versus pH data for clarifier effluent (Chapter 5, Section 4), i.e. where precipitation took place in the presence of high concentrations of sludge, was collected. A plot of the data in the form, $-\log [(Mg_T^{2+})(OH^-)^2]$ versus pH indicates that the activity product is independent of pH and has a relatively constant value of 10,5 (see Figure 6.6). From these results it is clear that the relationships given by Eqs.(6.9 and 6.10) between the $Mg(OH)_2$ activity product and pH are only apparent relationships, the reason being that precipitation has not proceeded to completion due to the absence of an adequate sludge concentration.

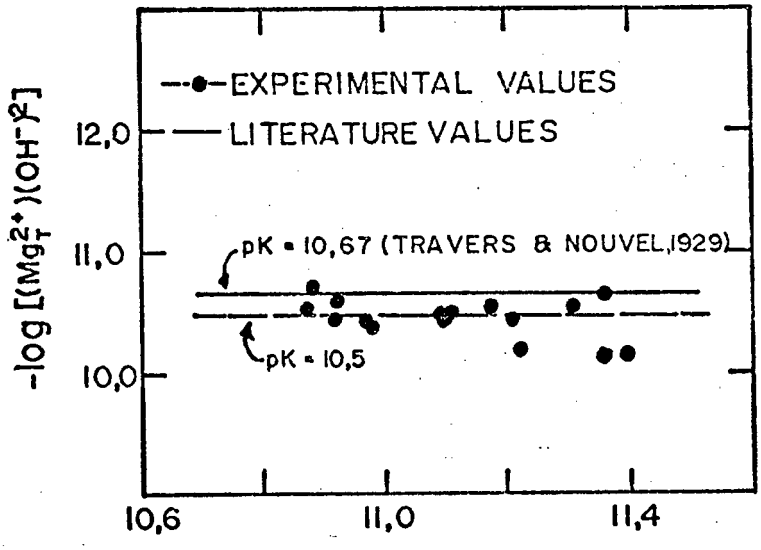

Figure 6.6. $Mg(OH)_2$ activity product values for full-scale plant clarifier effluent, indicating the independence of $pK_{Mg(OH)_2}$ from pH

There is no agreement in the literature on the solubility product value for pure synthetic magnesium hydroxide (see Chapter 2, Section 2.3). However, the experimentally determined $Mg(OH)_2$ activity product constant of 10,5 is in reasonable agreement with one of the solubility product values reported in the literature, i.e. the value determined by Travers and Nouvel (1929) for pure synthetic solutions, $p[AP(Mg(OH)_2] = 10,67$.

5.2 Recarbonated Effluent

The calcium carbonate solubility product for recarbonated lime-treated secondary effluent is expected to have a value between $10^{-6,7}$ and $10^{-8,3}$, i.e. the K_{CaCO_3} values for lime-treated secondary effluent and a synthetically pure calcite system, respectively, since a recarbonated effluent contains only trace concentrations of organic and phosphorous matter in comparison to secondary effluent.

A series of tests were conducted on the Stander Plant recarbonation unit to produce experimental values of $(Ca^{2+})(CO_3^{2-})$ values under a variety of test conditions, including different influent qualities, reactor pH values and temperature. The degree of recarbonation was varied stepwise to result in recarbonated effluent with pH values ranging from 11,0 to 9,5. The influent quality varied over the test period, average, maximum and minimum values being,

pH	- 11,35 (11,21 - 11,59)
Alkalinity (mg ℓ^{-1} as $CaCO_3$)	- 171 (129 - 244)
Calcium (mg ℓ^{-1} as $CaCO_3$)	- 180 (135 - 235)
Magnesium (mg ℓ^{-1} as $CaCO_3$)	- - (less than 10)
COD (mg ℓ^{-1} as O)	- - (10 - 20)
Ortho-Phosphate (mg ℓ^{-1} as P)	- - (less than 0,2)
Total Phosphate (mg ℓ^{-1} as P)	- - (0,5 - 1,5)
Temperature (^{o}C)	- 23,6 (20,3 - 27,1)

Snatch samples of recarbonated effluent were taken from the full-scale reactor, placed in 1ℓ glass bottles which were shaken mechanically for approximately 24 hours, after which the effluent was analysed for pH, temperature and dissolved calcium, magnesium, COD, total and ortho-phosphate and alkalinity. The samples did not contain inoculated seed sludge, since sludge was not recirculated to the primary recarbonation reactor.* Experimental and derived data generated during this series of tests is given in Appendix 13.

Experimentally derived $p[(Ca^{2+})(CO_3^{2-})]$ values as a function of pH are illustrated in Figure 6.7. From this plot it appears that the apparent pK_{CaCO_3} values are a function of pH in the pH range 8,3 to 10,5, and are constant at a value of 7,1 at pH values in excess of 10,5. This apparent pK_{CaCO_3} dependence on pH is analogous to the apparent $pK_{Mg(OH)_2}$ dependence on pH. Since K_{CaCO_3}, the calcium carbonate solubility product for recarbonated lime-treated secondary effluent, must be a true constant (for a constant temperature), the pH dependency is a false one and results due to undersaturated conditions being created by carbon dioxide addition in quantities exceeding requirements for optimum softening.

Changes in effluent quality on recarbonation may be predicted from Modified Caldwell-Lawrence Diagrams as illustrated in Figures 6.8(a-c). In these figures the constant parameter lines representing the average influent Alkalinity (3,42 mmol ℓ^{-1}) and calcium (1,80 mmol ℓ^{-1}) concentrations and pH = 11,3 are sketched in. On all three Diagrams (pK_{CaCO_3} = 6,7; 7,1; 8,35) the influent is shown to be oversaturated with respect to calcium carbonate. Given sufficient reaction time and contact with sufficient sludge a saturated condition will establish with the saturated effluent quality given by point B in Figure 6.8(a-c). Addition of carbon dioxide will effect further softening, resulting in effluents with qualities as given by points on the vertical line between B and C. Optimum softening is achieved by CO_2

*The recarbonation process sludge has a high $Fe(OH)_3$ content. It was thought at the time of the experiment that this may inhibit $CaCO_3$ precipitation and therefore the sludge was not recirculated to the primary recarbonation reactor.

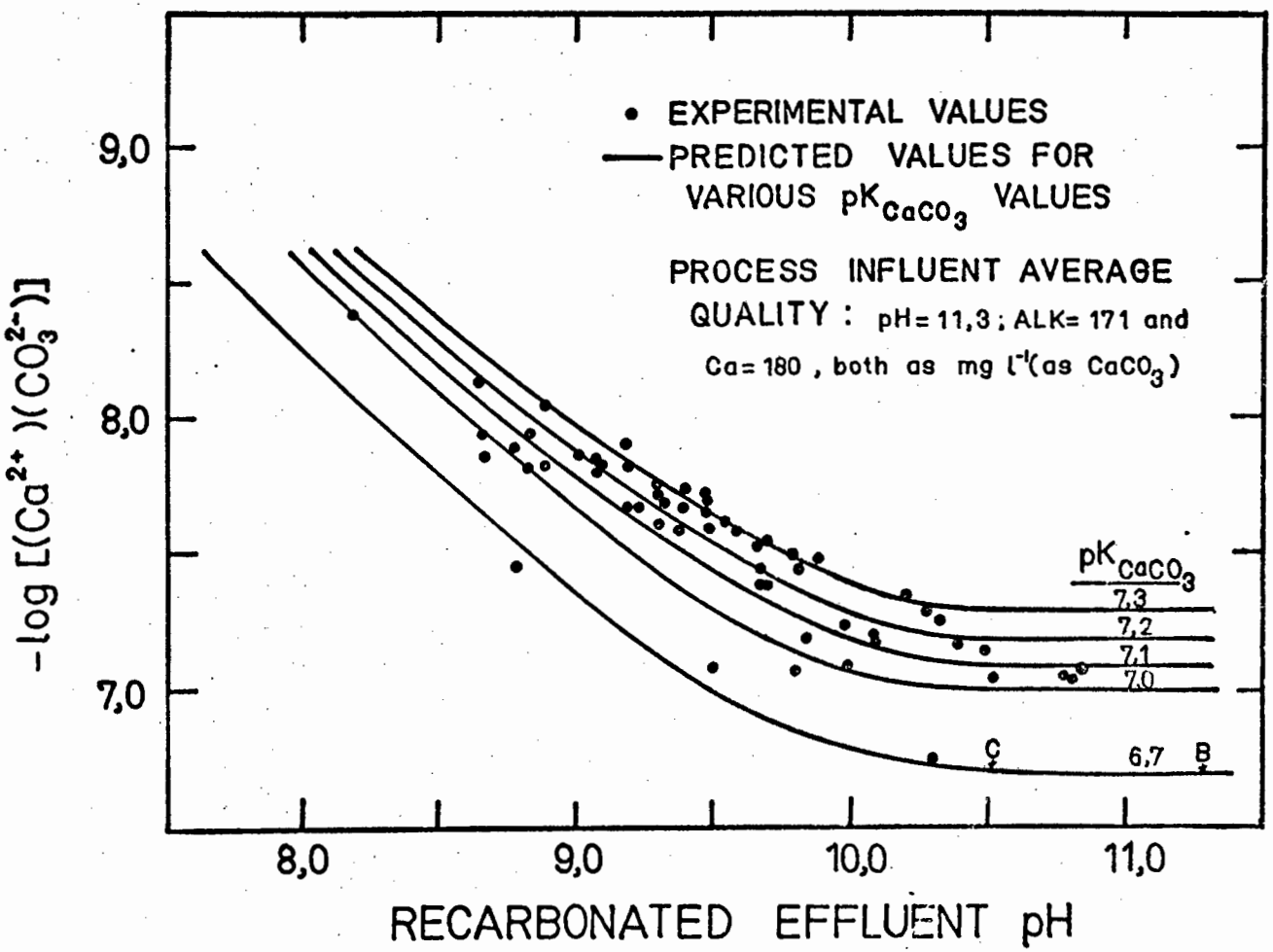

Figure 6.7. Experimentally derived and theoretically predicted relationships between pK_{CaCO_3} and pH for recarbonated lime-treated secondary effluent (full-scale tests - no sludge recirculation)

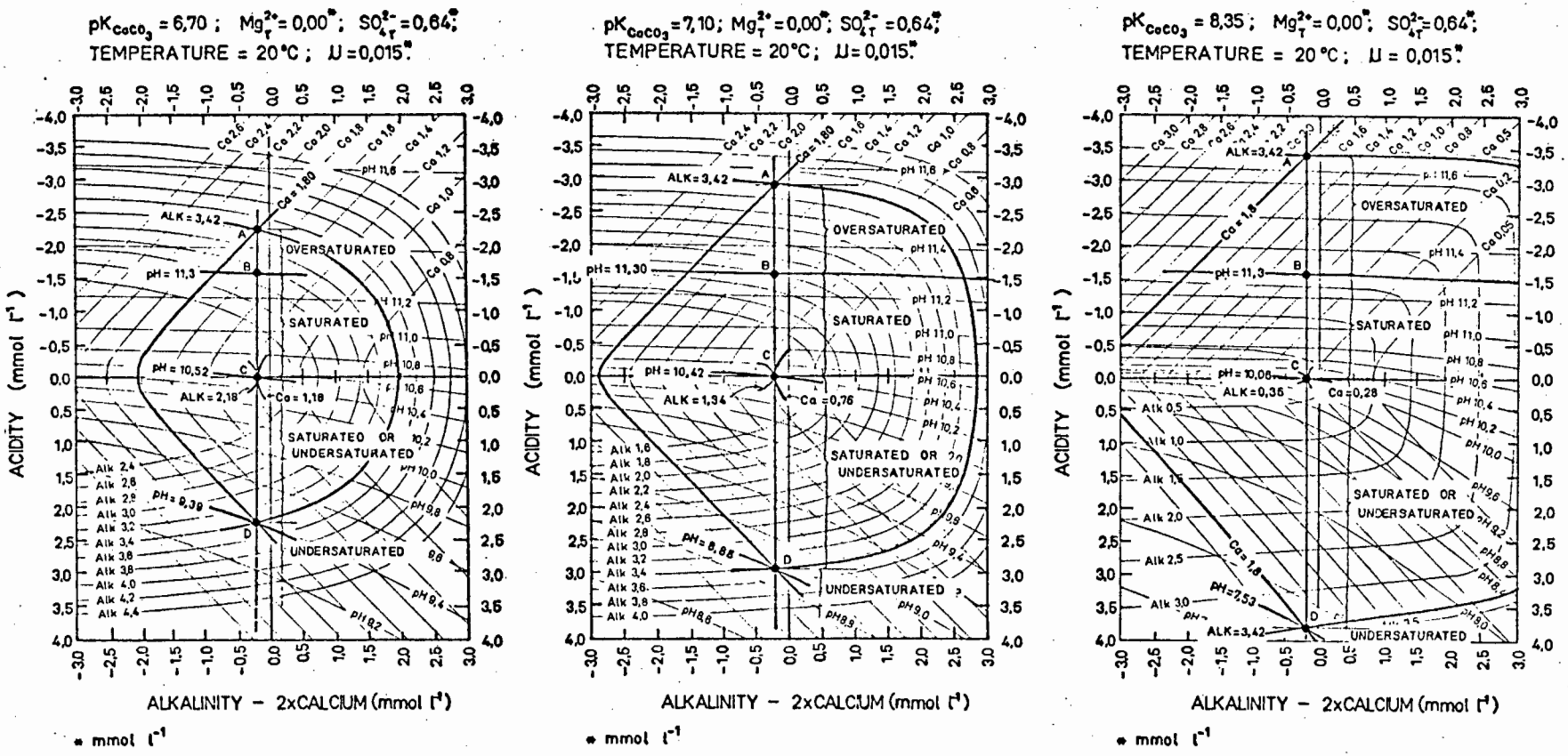

Figure 6.8(a-c). Modified Caldwell-Lawrence Diagrams for three different pK$_{CaCO_3}$ values, indicating the changes in effluent quality which take place on recarbonation

addition to point C. Should more CO_2 be added after the state given by point C is attained, the water will then be undersaturated and tend to dissolve $CaCO_3$.

Using Modified Caldwell-Lawrence Diagrams (Figures 6.8(a-c)) it is possible to predict the theoretical relationships between measured $p([Ca^{2+}][CO_3^{2-}])$ values and pH for different "true" calcium carbonate solubility product values, i.e. pK_{CaCO_3} = 6,7; 7,1 and 8,35 as shown in Figure 6.7. The experimentally derived $p([Ca^{2+}][CO_3^{2-}])$ values lie approximately within the plots of predicted $p([Ca^{2+}][CO_3^{2-}])$ vs pH for pK_{CaCO_3} = 7,0 to 7,3. The best-fit predicted plot for the pH range of importance for softening by recarbonation, pH 9,8 to 10,8, is obtained from a Diagram with pK_{CaCO_3} = 7,1. Figure 6.9 illustrates the validity of the choice of pK_{CaCO_3} = 7,1, i.e. approximately single point intersection of constant parameter lines for pH and Alkalinity and calcium concentrations.

It is interesting to note that the calcium carbonate solubility product for recarbonated effluent is approximately 1,2 orders of magnitude larger than the thermodynamic solubility product for calcite, i.e. $10^{-7,1}$ as compared to $10^{-8,3}$, indicating that even the trace quantities of organic and phosphorous matter present in recarbonated effluent still have a marked effect on the calcium carbonate solubility. The consequences of this high $CaCO_3$ solubility for recarbonated effluent are important for water reclamation. It indicates that it is not possible to reduce the calcium concentrations in reclaimed water to the low values consistent with a pK_{CaCO_3} value of 8,3, in fact for reclaimed water on the Stander Plant calcium concentrations of much under 80 mg ℓ^{-1} (as $CaCO_3$) do not appear to be attainable in the recarbonation process stage.*

*This depends to some degree on the amount of permanent hardness in the original influent.

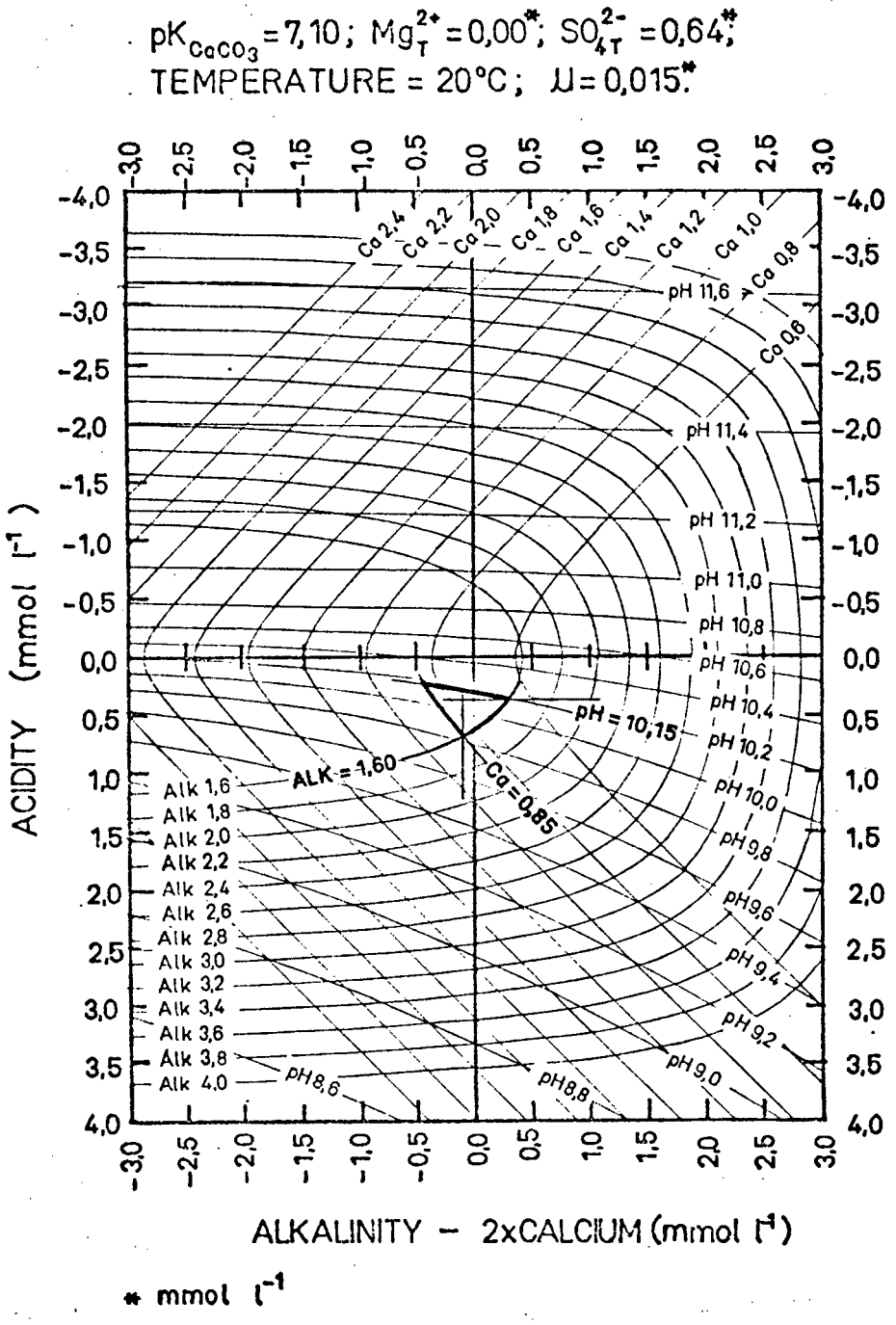

Figure 6.9. Plot of typical recarbonated effluent quality illustrating the validity of the choice of $pK_{CaCO_3} = 7,1$ for recarbonated-softened effluent

The data obtained in this single series of tests are specific to these tests. A different influent will modify the lowest calcium concentration attainable if the influent calcium, alkalinity and ammonia concentrations should change. Furthermore, it is not known in what degree recarbonated effluent solubility product constants will remain the same for different influent qualities arising from different organic and phosphorous material residual concentrations.

The observations reported above now raise an important aspect as to the behaviour of the reclaimed water after discharge from the plant. After recarbonation the water is sand filtered, chlorinated, passed through carbon adsorption columns and is finally stabilized with $Ca(OH)_2$. It is not known what effect these processes will have on the pK_{CaCO_3} value. Chlorination in particular may destroy some of the organic material in the water and carbon adsorption will physically remove all or most of the residual organics. If the pK_{CaCO_3} value is raised by these processes, it is possible that further $CaCO_3$ precipitation can take place in water reticulation systems if final stabilization is based on calculations with the lower pK_{CaCO_3} value of 7,2. This aspect has only become evident by the analysis made here and in fact no data is available on the stability of the final reclaimed effluent. It is evident that further work on this aspect is necessary.

6. APPLICATION

The $CaCO_3$ and $Mg(OH)_2$ activity product constant values may be used for predictive purposes in problems associated with lime treatment and recarbonation of secondary effluents. Incorporating these constants in the Modified Caldwell-Lawrence Diagram (dealt with in Chapter 4, Section 5) allows the prediction of the basic relationships which characterize lime-treated and recarbonated effluents, such as the relationships between pH and lime dosage, alkalinity, residual calcium and residual magnesium, and enables the lime and CO_2 requirements to be estimated knowing the initial constitution of the effluent.

7. GENERAL CONCLUSIONS

(1) Thermodynamic equilibrium with respect to calcite could only be attained in pure synthetic calcium carbonate solutions, in the presence of high concentrations of calcite (app. 10000 mg ℓ^{-1}) and with long reaction periods (24 hours).

(2) In lime-treated secondary effluent thermodynamic equilibrium with respect to calcite could *not* be established, notwithstanding seeding with high concentrations of pure calcite (app. 10000 mg ℓ^{-1}) and long reaction periods (>24 hours). However, the changes in $CaCO_3$ activity products were small after 24 hours and for practical purposes the activity products may be considered *constant*.

(3) Calcium carbonate activity product constant values for lime-treated secondary effluent were found to be independent of pH and temperature in the pH range 9,8 to 11,7 and temperature range 8 to 23°C. The average $p[AP(CaCO_3)]$ value is 6,8.

(4) Calcium carbonate activity product values for recarbonated effluents were found to be constant at the approximate value of $10^{-7,1}$. Data reported in the literature (and reported earlier in this investigation) which gives the pK_{CaCO_3} as a function of pH, was shown to be due to measurements on solutions undersaturated with respect to $CaCO_3$.

(5) Although the magnesium hydroxide activity product for lime-treated secondary effluent appeared to be a function of pH, it was shown that in full-scale plants this is in fact not the case if precipitation takes place in the presence of high sludge concentrations. The $Mg(OH)_2$ activity product is approximately constant at $10^{-10,5}$ for sludge blanket clarifier effluent at 20°C in the pH range 10,8 to 11,4.

(6) It was demonstrated that the $CaCO_3$ and $Mg(OH)_2$ activity products for lime-treated secondary effluent, when incorporated in the Modified Caldwell-Lawrence Diagram, may be usefully applied for predicting the basic relationships characterizing lime-treated effluents, i.e. the relationships between pH and lime dosage, residual alkalinity, calcium, magnesium and sludge generated.

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CHAPTER 7

PROCESS DESIGN GUIDELINES FOR PRECIPITATION IN WATER RECLAMATION SYSTEMS

1. INTRODUCTION

The basis for process design for precipitation as utilized in water reclamation systems was developed from the established technologies for flocculation and softening of surface waters. However, application of lime treatment and recarbonation processes to secondary effluents gave rise to some specific problems to which there was no background of experience. Some of these problems have been solved from experience gained on existing reclamation plants. When reviewing this experience it is evident that the major problem which still limits optimal design is a lack of knowledge of precipitation phenomena. This lack of knowledge has resulted in designs in which the reactor volumes are not optimal; points of chemical addition are wrongly located; lime solubilization is below maximum efficiency and scale formation in pipes, pumps, reactors, ammonia stripping towers and sand filters is commonly encountered.

The work reported in the previous chapters has pinpointed the causes of many of these problems and it is now possible to set up some guidelines which should lead to improved process design. The accent is on process design for lime treatment. Process design for recarbonation is also dealt with, but in lesser detail. In addition a number of design features are proposed for minimizing scale formation. No guidelines are given for structural design. Other processes which may form part of the reclamation system, such as influent quality equalization, ammonia stripping, sand filtration, chlorination, ozonation and carbon adsorption are not dealt with.

In the design of a water reclamation system there may be considerations over-riding the optimal design of any specific unit process, for example :

An experimental investigation may indicate that the concentration of Mg^{2+}_T is very low and does not warrant removal. In that event it may only be necessary to apply lime treatment to achieve a pH of say 10,4, which may be sufficient for the removal of ortho-phosphate, organic matter and carbonate hardness. However, by utilizing a pH of 10,4 the efficiency of pathogen removal will be greatly reduced and hence the relative fraction of pathogens removed by filtration and chlorination will have to be increased. This may not be acceptable and it may be specified that lime treatment upto a pH of 11,2 is essential.

There may be other considerations of this kind that impose limitations on the process design. It is not possible to deal with all of these within the scope of this investigation. Therefore, the approach followed in this chapter is that the precipitation aspects of the process will be designed to embrace the effective removal of carbonate hardness, magnesium, ortho-phosphate, organic matter and ammonia (by air stripping). Other factors which may impose limitations on the process are not considered.

For information on the wider aspects of design the reader is refered to the works of : Culp, Wesner, Culp and Benjes (1975); Van Vuuren and Henzen (1972); Hartung (1972); Stander and Van Vuuren (1969); Cillié (1975); Mennell, Merrill and Jorden (1974); Jenkins and Lee (1976); and Van Vliet, Wiechers and Hart (1977).

2. DESIGN SEQUENCE

"Ideally" a process design for lime treatment or recarbonation should comprise the following steps,

(1) Determine the chemical and physical quality of the untreated water (see Section 3.1). Specific attention should be given to extreme diurnal and seasonal variations in quality.

(2) From preliminary observations predict the response of the water to chemical treatment by means of some theoretical model, for example the Modified Caldwell-Lawrence Diagram. This step will provide estimates of the effluent lime demand, inorganic quality of the treated effluent, sludge production rate, etc. These predicted values give the designer certain crucial information before embarking on laboratory and pilot plant studies.

(3) Conduct a laboratory investigation to verify predictions made in (2) above and characterize the process behaviour of parameters which cannot be predicted, for example organic matter and turbidity removal.

(4) Design and operate a pilot plant to verify or modify the proposals for the unit process design developed under (3) above.

(5) Design a full-scale process system based on the information obtained under (3) and (4) above.

In practice it may not be possible to adhere to this "ideal" design sequence. Considerations such as, available finance, time, plant size and previous experience regarding both the process and the type of effluent to be treated, will dictate the extent of the design investigation. For the design of a works of say 50 Mℓ d^{-1} or larger, extensive laboratory and pilot scale investigations may be justified. However, for a smaller plant of say 5 Mℓ d^{-1} or less, only laboratory investigations and limited pilot plant tests may be justified. In the latter case, optimal design will not be possible and additional safety factors will have to be incorporated into the design. These safety factors should include :

(1) Sufficient reaction time in reactor.
(2) Variable sludge recirculation rates.
(3) Variable chemical dosing points, etc.

3. LIME TREATMENT

The design sequence as set out in Section 2 above is dealt with in detail for lime treatment in this section.

3.1 Characterization of the Effluent to be Reclaimed and Decisions Regarding Related Process Selection

Characterization of the effluent to be reclaimed is essential in order to have information on the parameters which affect the lime treatment and other unit processes. There are two major aspects which need to be considered :

(1) the average chemical and physical quality of the effluent, and

(2) the daily and seasonal variation of this quality.

The chemical and physical quality of an effluent can be assessed from the following tests : Concentrations of calcium, magnesium, total alkalinity, total dissolved solids, soluble and total chemical oxygen demand (COD), phosphorous species (ortho- and organic phosphates), nitrogenous species (ammonia and organic nitrogen) pH, temperature and turbidity. These parameters comprise a comprehensive analysis of the effluent and should be performed on a 24 hour composite sample in order to give information on the average daily quality of the water.

The daily quality variations may be assessed by analyzing samples taken at regular intervals over 24 hours. The comprehensiveness of the testing may be reduced to measuring only pH, NH_4, COD and total alkalinity, as these parameters can vary appreciably over 24 hours and have a significant influence on the process, either directly or indirectly. Such a set, or preferably sets, of samples should be taken on those days where the records of the biological plant indicate the worst quality effluent in order to establish effluent quality during extreme conditions.

With regard to seasonal variations of effluent quality, this may also be assessed from records of the effluent quality from the biological system. If time allows, the average quality in the different seasons of the year should be determined as described above.

Except in very special circumstances where the quality is very uniform, i.e. having variations of less than 10 percent about the mean, it is recommended that the quality should be smoothed out by the incorporation of an equalization basin. From tests conducted on the Stander Plant under constant flow conditions, an equalization basin with a hydraulic retention time of 12 hours reduced daily variation of quality to 30% of the variation in the influent quality (Van Vliet, Wiechers and Hart, 1976). To determine the size of a basin required for reducing the variation in quality to some desired value, a paper by Gutoff (1956) may be consulted. Should equalization of flow be required reference should be made to papers by La Grega and Keenan (1974), Speece and La Grega (1976), Wallace (1968) and an EPA

publication (1974).

Another critical decision which must be made based on the reclamation plant influent quality, is the influence of the ammonia concentration on unit process selection (Van Vuuren, 1977),

(1) *If the ammonia concentration is consistantly less than about 5 mg ℓ^{-1} (as N)* - no provision for ammonia stripping need be made. The removal of these low levels of ammonia can be accomplished economically by breakpoint chlorination. In most biofilter plants this objective can hardly be met, particularly during winter months.

(2) *If the ammonia concentration ranges between approximately 5 to 8 mg ℓ^{-1} (as N)* - removal down to 5 mg ℓ^{-1} can be accomplished by stripping in surface aerated equalization basins. In this event lime treatment must preceed the equalization basin and the pH of the water in the basin should of necessity be maintained above pH 10,8. The basin must be equipped with mechanical surface aerators.

(3) *If the ammonia concentration is greater than about 8 mg ℓ^{-1} (as N)*- an ammonia stripping tower needs to be incorporated following the equalization basin as in (2) above.

The need for ammonia stripping using quality equalization basins in combination with or without stripping towers will, however, depend on a critical assessment of factors related to seasonal ammonia concentration variations, power and chlorine costs, and quality objectives for reclaimed water.

3.2 Predictions Using the Modified Caldwell-Lawrence Diagram

Once the chemical and physical quality of the effluent to be reclaimed and its daily and seasonal variations have been determined, predictions regarding the effluent's response to lime treatment may be made using a Modified Caldwell-Lawrence Diagram with pK_{CaCO_3} = 6,7 and $pK_{Mg(OH)_2}$ = 10,5. The following basic characterizing relationships may be predicted :

(1) lime dosage as a function of pH,
(2) residual total alkalinity as a function of pH,
(3) residual total dissolved calcium as a function of pH,
(4) residual total dissolved magnesium as a function of pH, and
(5) sludge generated as a function of pH.

A comprehensive description of the Modified Caldwell-Lawrence Diagram and its use is given by Loewenthal and Marais (1976) in their book "Carbonate Chemistry of Aquatic Systems - Theory and Application". Appendix 1 also details in short point form the application of the Diagram to problems related to the lime treatment of effluents.

Example

The following daily average chemical quality was measured for a Pretoria Sewage Works secondary effluent,

pH - 7,64
Total alkalinity (as $CaCO_3$) - 163
Calcium (as $CaCO_3$) - 103
Magnesium (as $CaCO_3$) - 91
Ortho-phosphate (as PO_4-P) - 6,2
COD (as O) - 25
Ammonia (as NH_3-N) - 5,1
Total Dissolved Solids - 450
Temperature - 20°C

Using a Modified Caldwell-Lawrence Diagram (incorporating ion-pairing effects) with,

Temperature - 20°C
Ionic strength - 0,015
pK_{CaCO_3} - 6,7
$pK_{Mg(OH)_2}$ - 10,5

the five basic characterizing relationships previously listed were determined and are illustrated in Figures 7.1 to 7.5.

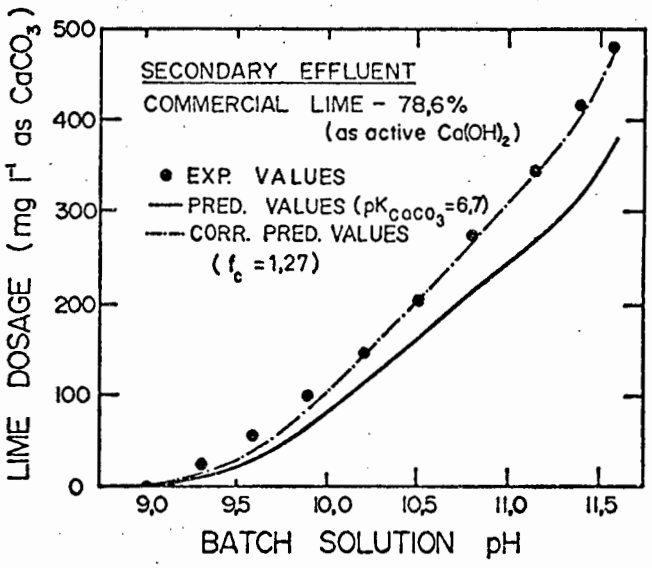

Figure 7.1. Predicted and experimentally determined relationships between lime dosage and pH for a laboratory batch system with a high concentration of seed sludge

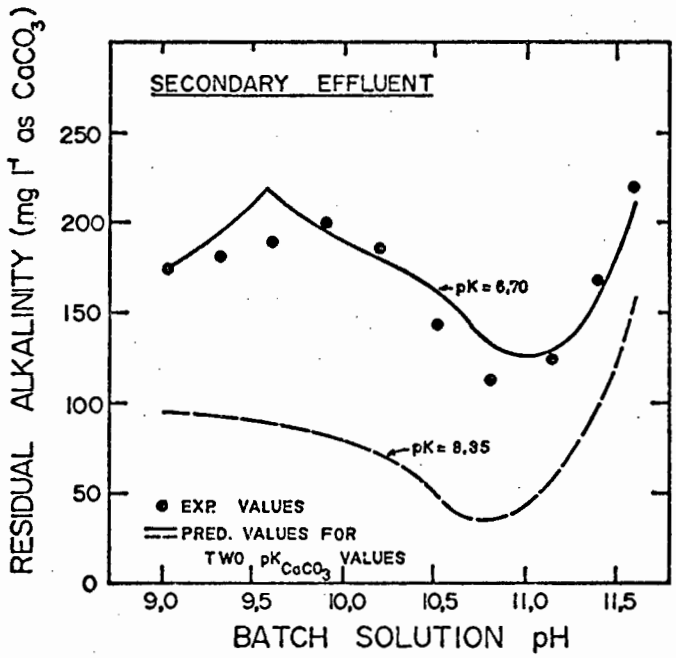

Figure 7.2. Predicted and experimental relationships between residual Alkalinity concentration and pH.

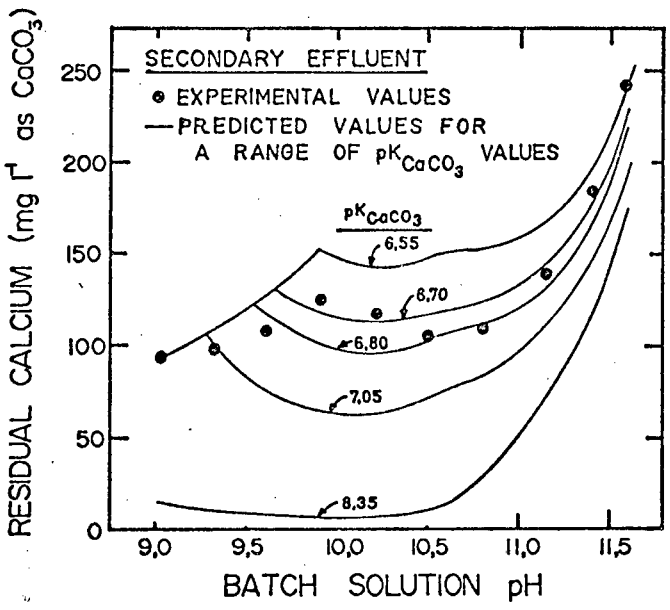

Figure 7.3. Predicted and experimental relationships between residual calcium concentration and pH

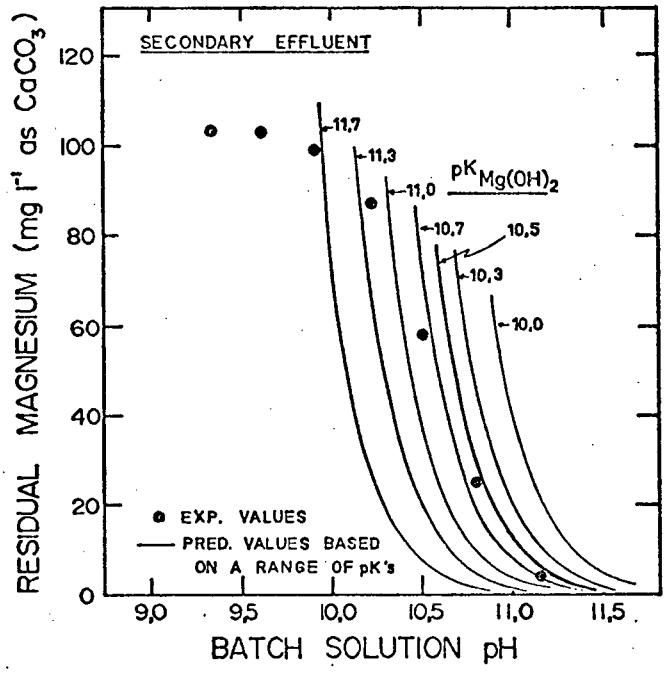

Figure 7.4. Predicted and experimental relationships between residual magnesium concentration and pH

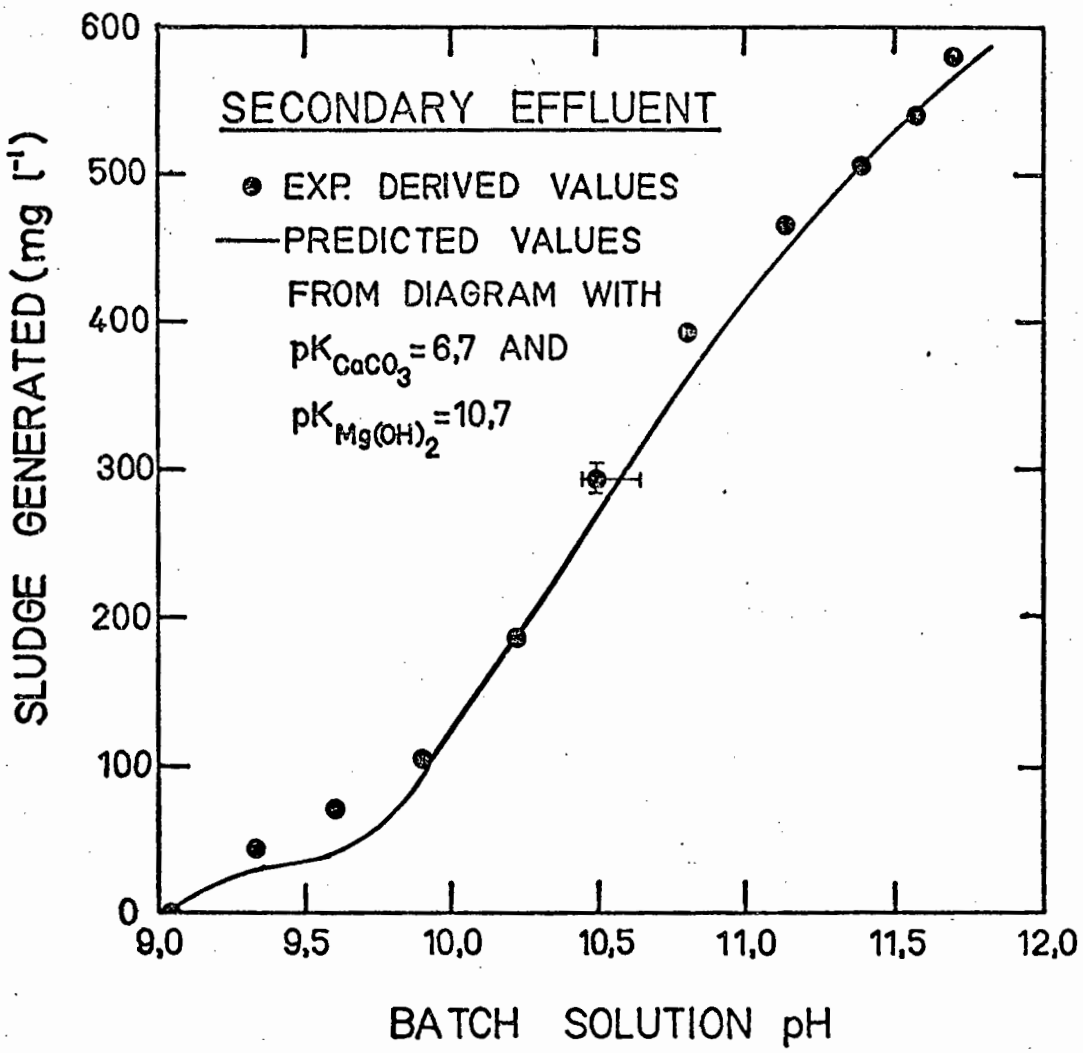

Figure 7.5. Experimentally derived and predicted values for mass of sludge generated as a function of pH

Using the predicted characterizing relationships, conclusions may be made regarding the following questions,

(1) What lime dosage should be applied to achieve certain specified objectives, i.e. to produce an effluent with a specific pH, to affect optimal calcium, alkalinity, magnesium or total hardness removal, etc?

(2) What quantities of sludge will be generated by lime addition to achieve the specific objectives listed in (1) above?

(3) On the basis of (1) and (2) above, is lime treatment a suitable water treatment process for this particular effluent?

(4) If lime treatment is to be more fully investigated, what range of lime dosages or pH-values should be considered?

3.3 Laboratory Investigations

The first step in a laboratory investigation is to assess the response of the effluent to be reclaimed to lime treatment in a series of batch tests commonly referred to as *jar tests*.

3.3.1 Jar tests

Jar tests for assessing the effects of lime treatment may be conducted as follows :

(1) Place 2ℓ effluent in a glass beaker.

(2) Add a preselected amount of lime to the effluent in the form of a 5 percent slurry over a period of one minute, while intensively agitating the solution using a magnetic stirrer or paddle stirrer at approximately 100 r.p.m. Slow lime addition to an intensely mixed effluent is necessary to prevent localized high pH values.

(3) Add 200 mℓ of a 5 percent preformed sludge slurry (prepared by treating 50 ℓ of effluent with lime to a pH of say 11,0).

(4) Continue mixing the solution intensely for four minutes. This will result in essentially complete lime dissolution and precipitation reactions. Coagulation reactions will also take place during this period.

(5) Reduce the mixing intensity to maintain just sufficient agitation to keep the precipitates from settling out of solution (app. 40 r.p.m. for paddle stirrers). Maintain this low intensity mixing for 10 minutes. This stage in the test is required for flocculation of the precipitates.

(6) Withdraw a 20 mℓ sample for subsequent total calcium analysis. Stop the stirring device and allow the flocculated precipitates to settle for 30 minutes. Observe the floc size during settling. Determine the rate of solids settling by withdrawing small samples of treated effluent 20 mm below the solution surface every 2 minutes over the 30 minute settling period. Analyse these samples for turbidity and total ortho-phosphate.

(7) Analyse the supernatant for residual total alkalinity, dissolved calcium, magnesium, ortho-phosphate, COD, ammonia, turbidity and pH.

(8) Special care should be taken to ensure minimal contact between the alkaline solutions (lime slurry and lime-treated effluent) and the air, by having air-tight covers or using a nitrogen blanket over the solution-air interfaces. Neglect of this aspect may result in reaction between the hydroxide ions of the alkaline solutions and CO_2 in the air, resulting in carbonate ion formation and ultimately $CaCO_3$ precipitation. This phenomenon will give rise to an undue high lime demand and additional sludge.

If a thorough investigation is intended, a wide pH range should be considered, say 8,0 to 11,6, in pH increments of approximately 0,3 to 0,5. Plot experimentally determined residuals as a function of pH. Typical results are shown in Figure 7.6 (a-d). Some experimental and

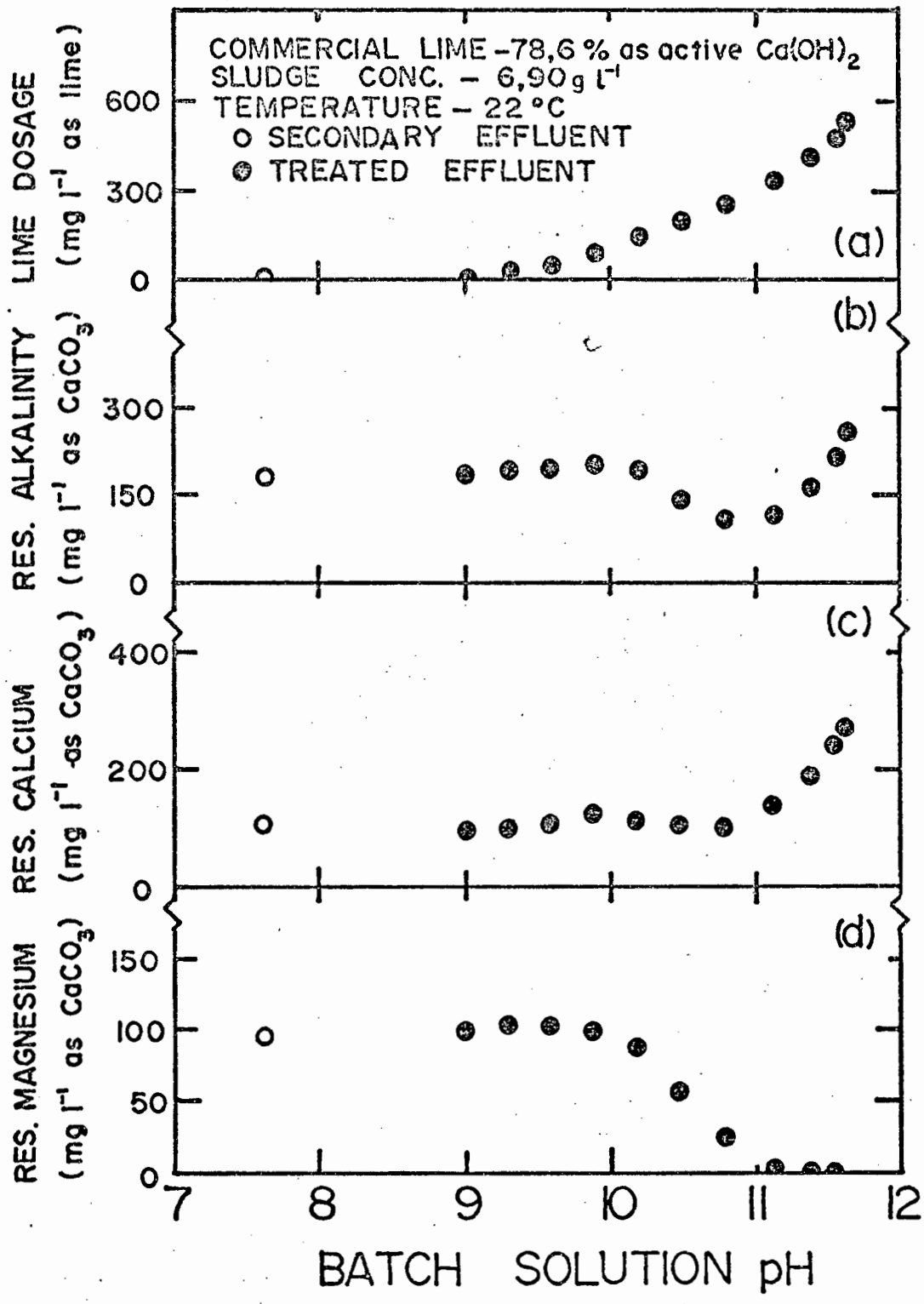

Figure 7.6. Response of secondary effluent to lime treatment in the presence of high concentrations of seed sludge (Jar-test results)

predicted results are illustrated in Figures 7.1 to 7.5 indicating the accuracy of predictions possible by using a Modified Caldwell-Lawrence Diagram.

Conclusions and decisions from the preliminary jar tests

(1) *pH versus lime dosage* - This relationship will be used to determine the lime dosage required for obtaining any specific pH.

(2) *pH versus residual magnesium* - This relationship will be used to determine the minimum pH for obtaining any desired magnesium residual.

(3) *pH versus residual calcium and ortho-phosphate* - These relationships will be used to determine the pH at which the desired removal of calcium hardness and ortho-phosphate takes place.

(4) *pH versus residual turbidity* - This relationship will be used as a rough guide to determine the pH at which coagulation, flocculation and sedimentation proceed satisfactorily.

(5) *pH versus sludge generated* - This relationship will be used for predicting the mass of sludge generated at any specific pH.

At this stage of the jar test investigation a preliminary decision must be made regarding the pH, or pH-range, at which a more intensive jar test investigation is to be conducted. To come to this decision consider the objectives for utilizing the lime treatment process, i.e.

(1) ortho-phosphate removal,
(2) COD removal,
(3) suspended solids and turbidity removal,
(4) ammonia removal,
(5) magnesium removal, and
(6) carbonate hardness removal.

Having decided which of these objectives has to be attained, and usually it is required that all these objectives be met, list the minimum pH for achieving each of these selected objectives from the jar test results. The highest pH value on this list will determine the pH to be attained by lime treatment for the specific water under consideration.

Usually the highest pH required in lime treatment is determined by magnesium removal considerations, i.e. pH values in the range 11,2 to 11,6. Magnesium removal from solution is achieved by magnesium hydroxide precipitation. This salt precipitates in the form of a floc and provided there is sufficient magnesium in the water, i.e. more than about 80 mg ℓ^{-1} (as $CaCO_3$), these flocs will aid in the clarification of the lime-treated water. Thus magnesium removal and satisfactory clarification may be inter-related.

Should magnesium removal not be an objective for the specific application under consideration, the next consideration is usually the pH required for ammonia stripping. pH values in excess of approximately 10,8 are required for this purpose (see Chapter 2, Figure 2.14). Operating the lime treatment process at this pH may result in unsatisfactory clarification. Should this occur the application of flocculant aids such as ferric salts, activated silica or polyelectrolytes must be investigated (see later).

Should ammonia removal not be an objective for this specific application, the next consideration most probably will be carbonate hardness removal. The pH for optimum carbonate hardness removal (as $CaCO_3$) is obtained from the jar test results and is usually in the pH range 10,0 to 10,8. Again, clarification most probably will have to be aided by flocculant aids.

Should the only objectives of the treatment be ortho-phosphate and COD removal, low pH operation in the pH range 9,5 to 10,5, most probably will be required. The minimum pH value to achieve these removals is obtained from the jar test results. Again, flocculant aids may have to be considered.

Once the decision has been made regarding the pH (or pH range) necessary to achieve all the specified objectives for the treatment, further jar tests can be made to determine the effect of temperature, reaction time and sludge on the precipitation reactions. The relative efficiency of various flocculant aids in clarifying treated water may also be studied by means of jar tests.

(1) *Temperature* - Normal practice is to conduct the above described jar tests at the reigning temperature(s) expected in the plant. Should widely differing temperatures be expected, say for summer and winter conditions, duplicate sets of jar tests are suggested for the two extreme temperatures.

(2) *Reaction Time* - The effect of reaction time on precipitation reactions may be studied using the jar test procedure. However, this is not commonly done since in practice continuous reactor systems are used rather than batch reactor systems (such as the jar test), and the result for these two systems are often significantly different. The effect of reaction time on the precipitation reaction is therefore studied in continuous precipitation systems (see later).

(3) *Sludge Concentration* - Conduct jar tests with a fixed quantity of lime to result in a selected pH value determined from the lime dosage versus pH curve. Add a range of different sludge masses to result in sludge concentrations from 1 000 to 15 000 mg ℓ^{-1}. (The sludge which is used in these experiments is produced by taking a large volume of effluent (app. 50 ℓ) and treating it with lime to a selected pH). The jar tests are conducted as before, except that sludge is added to the reaction mixture immediately after the lime addition stage. Determine the optimum sludge concentration for the lime-effluent reaction system under study, i.e. the minimum sludge concentration required for maximum calcium and magnesium removal.

(4) *Flocculant aids* - Once the optimum pH (lime dosage) and sludge concentration have been established, flocculation aspects should be considered. It is possible to ascertain if flocculant aids are required for improving turbidity removal and settling rate at the jar test level. The natural flocculation efficiency of lime-treated effluent is dependent on the presence of Mg^{2+} ions. If the magnesium ion concentration is low, such as is characteristic of effluents derived from soft waters (e.g. natural waters of the Western Cape in South Africa) the function of Mg^{2+} must be substituted by addition of other flocculant aids. It must be realised that optimum flocculant aid dosages for clarification can only be realistically estimated at the pilot-scale or full-scale level. Detailed procedures for screening and selecting flocculants using jar tests have been reported by Benedek and Bancsi (1977) A typical range of poly-electrolytes, their chemical composition, properties and performance are listed in Table 7.1. Performance evaluation results for a few of these poly-electrolytes are illustrated in Figure 7.7.

Table 7.1

Characteristics of various poly-electrolytes
(After BENEDEK and BANCSI, 1977)

Ionic Charge	State	Molecular Weight*	Chemical Composition	Dosage mg/l	Performance %R	Performance u
cationic	solid	very high	Acrylamide and diethylaminoethylacrylate	0.2	91.0	640
cationic	solid	very high	Polyacrylamide based	0.2	91.5	600
cationic	solid	very high	Polyacrylamide based	0.2	38.0	520
cationic	solid	ultra high	Acrylamide and MTMMS***	0.2	93.0	500
nonionic	liquid	----------	Polyacrylamide	0.5	92.0	490
anionic	liquid	----------	Polyacrylamide (30% hydrolyzed)	0.5	81.5	480
cationic	liquid	low	Polyalkyl polyamine	0.8	79.5	480
cationic	liquid	low	Polyalkyl polyamine	0.8	86.0	480
anionic	liquid	----------	Polyacrylamide slightly hydrolyzed	0.5	93.5	465
cationic	liquid	low	No information	0.8	83.0	400
cationic	solid	high	Polyaminocarbonicacid ester	0.2	90.5	310

* Molecular Weights

ultra high: $8 \times 10^6 - 15 \times 10^6$
very high : $3 \times 10^6 - 8 \times 10^6$
high : $1 \times 10^6 - 3 \times 10^6$
low : $0 - 1 \times 10^6$

** %R: % removal
u: maximum permissible overflow rate for 90% floc removal in igpd/ft^2

*** methocrylaylexyethyltrimethyl-ammonium methyl sulfate

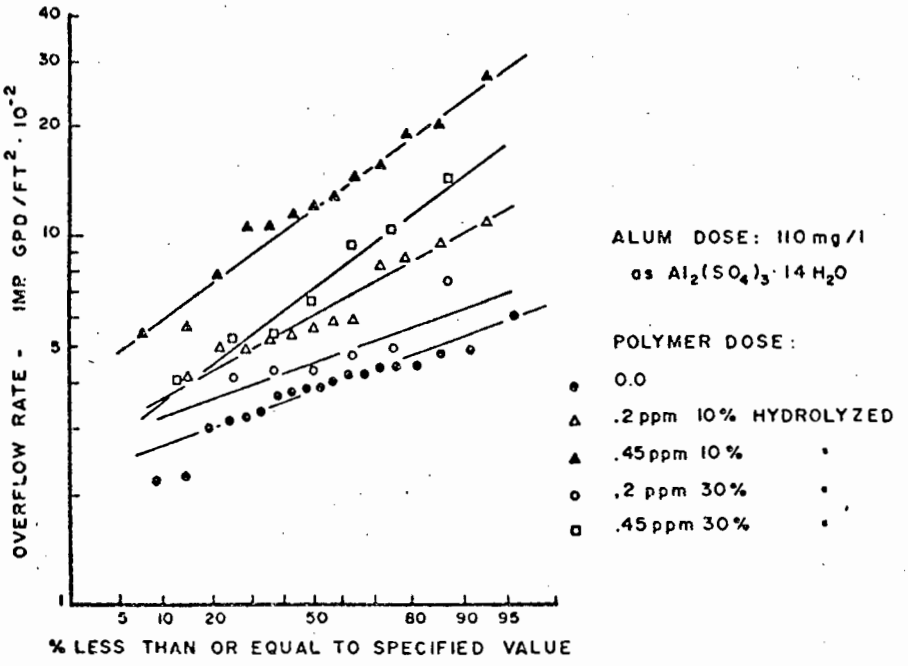

Figure 7.7. Plots of maximum permissible overflow rates for 90% of ultimate phosphorus removal from Napanee raw sewage (After BENEDEK and BANCSI, 1977)

Batch tests described above serve to establish the process behaviour under specific conditions of lime treatment. The dosage (or range of dosages) of lime, sludge and flocculant aid to achieve a treated water conforming to predetermined specifications or objectives, may thus be established. Unfortunately batch tests do not simulate the conditions prevailing in practical continuous processes. For this reason it is highly advisable also to undertake bench-scale tests with continuously stirred tank reactor (CSTR) systems.

3.3.2 Bench-scale CSTR tests

Bench-scale CSTR tests are conducted to verify or modify, where necessary, the process design information obtained from batch tests. The CSTR system simulates the actual full-scale continuous process.

The major difference between batch (Jar tests) and CSTR tests is that the conditions in the batch test are continuously changing due to the progression of the precipitation reactions with time, whereas in the CSTR system a steady state condition is maintained, usually close to the final equilibrium state depending on the residence time and other kinetic factors.

A flow diagram of equipment necessary for CSTR tests is shown in Figure 7.8. A brief description of suggested equipment is given in Table 7.2. Note that many variations are possible, depending on equipment already available. However, certain critical aspects relating to this equipment should be observed :

(1) *Effluent centrifugal pump* - Centrifugal pumps have stable characteristics only when running near or at their maximum delivery rate. For this reason, reducing flow by throttling with a valve will result in unstable flow. To overcome this problem the pump should be operated near its maximum pumping rate by means of recirculated flow (see Figure 7.8). Only part of this recirculated flow stream is used as actual effluent delivery. Control in such a system is attained by adjusting two valves until a desired effluent delivery flow is achieved.

(2) *Lime slurry pump* - The lime slurry flow rates required at bench scale are relatively low, e.g. 5,0 to 25,0 mℓ min^{-1}. Experience has shown that the only type of pump which will accurately deliver slurries at such low flow rates is a peristaltic pump. Care must be taken that the connecting tubing is of small diamter, ensuring high flow rates to prevent solids from settling out in the tubes. Clear and soft P V C tubing should be used, since in such tubes blockages can be visually observed and easily cleared by pinching.

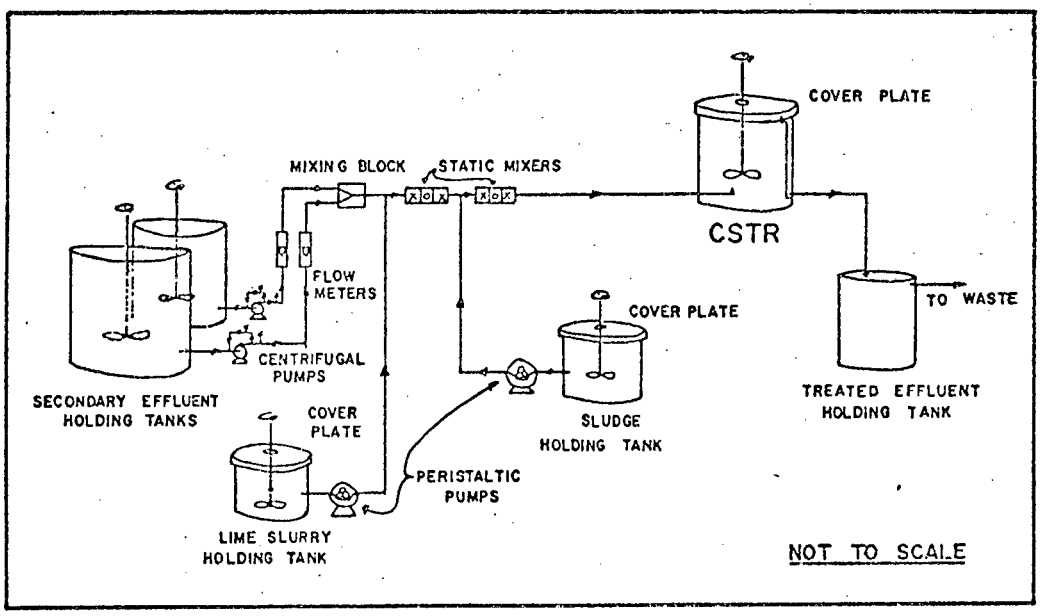

Figure 7.8 Flow diagram of equipment used in CSTR tests

(3) *Sludge pump* - The same holds for the sludge pump as described for the lime slurry pump in (2) above, except that the flowrates are somewhat higher, e.g. 50 to 200 mℓ min^{-1}.

(4) *Holding tanks* - The tanks should have covers to minimize air renewal over the solution surfaces.

(5) *CSTR* - The CSTR should preferably be a unit with a height to radius ratio of one, i.e. minimal surface to volume ratio and hence minimum area for scale formation. The unit should have vertical baffles along its sides (see Figure 7.9) and a lid to minimize air renewal over the solution surface. The effluent-lime mixture should enter the unit at the point of greatest turbulence to ensure rapid dispersion, e.g. under the mixing device just off centre. The effluent draw-off point should be away from the reactor influent point, e.g. a surface weir for effluent withdrawal is satisfactory.

Table 7.2

Suggested equipment for CSTR tests

Unit		Description
Effluent holding tank	-	200 ℓ, fibre glass
Effluent pump	-	max. delivery 5 ℓ min^{-1}, centrifugal
Effluent flow meter	-	0-3 ℓ min^{-1}, "Rotameter" type
Lime slurry holding tank	-	5 ℓ, fibre glass
Lime slurry agitator	-	high speed blade type or paddle-stirrer (100 r.p.m.)
Lime slurry metering pump	-	0-25 mℓ min^{-1}, peristaltic type
Sludge holding tank	-	50 ℓ , fibre glass
Sludge agitator	-	paddle stirrer (± 50 r.p.m.)
Sludge metering pump	-	50-200 mℓ min^{-1}, peristaltic type
Static mixers	-	2x six segment (5mm diameter)
CSTR	-	1 ℓ perspex unit or other (Figure 7.9)
CSTR agitator	-	paddle stirrer (Figure 7.9)
Treated effluent holding tank	-	200 ℓ, fibre glass.
Effluent transport tubing	-	5 mm clear, soft PVC tubing

The above dimensions, volumes, etc., are based on an effluent flow rate of 0,5-2,0 ℓ min^{-1}, lime slurry concentration of 2,5-5,0% and sludge concentration of 10 g $ℓ^{-1}$.

CSTR tests should be conducted for a range of lime dosages (reactor pH values), CSTR residence times, sludge concentrations and temperatures. Since a large number of permutations and combinations of the above four parameters are possible, some are usually chosen to be con-

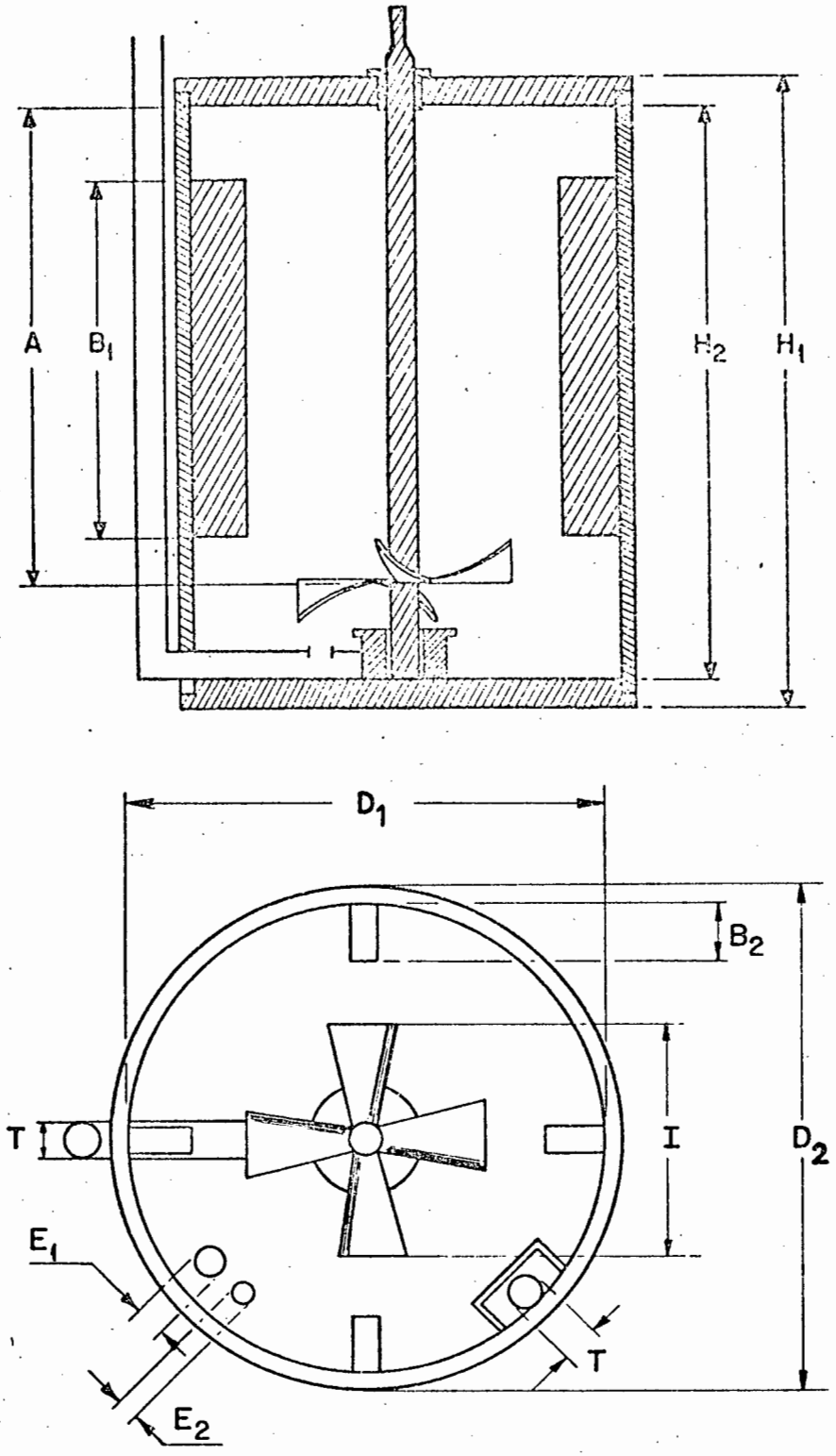

Figure 7.9. Elevation and plan of CSTR
(For dimensions see Appendix 5)

stant, e.g. temperature and sludge concentration are chosen to be constant and lime dosage and residence time are varied to establish the values of these variable parameters required to achieve a desired result. Reaction times should be related to temperature and the process design should ultimately be based on extreme winter conditions, since during winter the effluent quality is poor and the effluent temperature is low, both factors resulting in slower precipitation reactions.

A CSTR test run is conducted as follows :

(1) Prepare 50 ℓ sludge as previously described under the jar test procedure (Once CSTR runs have been completed, the resultant sludge may also be used). Fill the sludge holding tank with the sludge and switch on the paddle stirrer to ensure a homogeneous sludge. Calculate the flowrate of sludge required to achieve the desired sludge concentration in the reactor. Calibrate the sludge metering pump and set it to deliver this particular flow rate. Ensure that a cover is placed over the holding tank to minimize CO_2 absorption from the air.

(2) Make up a 5 percent lime slurry by adding commercial grade lime to effluent in the slurry holding tank. Switch on the paddle stirrer to ensure a homogeneous lime slurry. Calculate the approximate flowrate of lime slurry required to achieve the desired lime-effluent reaction mixture pH. Calibrate the lime slurry metering pump and set it to deliver this particular flowrate. Frequent adjustments of this pump setting are usually required to maintain a constant pH. Ensure that a cover is placed over the holding tank to minimize CO_2 absorption from the air.

(3) Fill the raw water holding tank with freshly collected effluent from the sewage works. If the effluent contains suspended matter, as it does in most cases, provision should be made for paddle

stirring in this unit to ensure a homogeneous solution.

(4) Switch on the raw water pump and adjust the flow control valve on the flow meter until a steady pre-selected flowrate is achieved. The flowrate and the CSTR volume determine the water residence time in the CSTR. Switch on the lime slurry and sludge metering pumps.

(5) Switch on the paddle stirrer in the CSTR. The mixing intensity should be relatively high ($\bar{G} \simeq 650\ sec^{-1}$) to ensure efficient lime dissolution, and intimate mixing of sludge with the CSTR contents and to prevent localized high pH conditions. Monitor the pH in the CSTR and adjust, if necessary, the lime slurry flowrate to maintain a constant pH.

(6) Run the lime-treated effluent into a holding tank. Sludge for subsequent experiments may be taken from this tank by first decanting the supernatant from the settled precipitates.

(7) Once steady state conditions have been established, as indicated by a constant pH in the CSTR, allow the continuous treatment to operate for a minimum of 3 CSTR residence times before sampling from the treated effluent. Analyse for total alkalinity, total and dissolved calcium, magnesium and ortho-phosphate, COD, suspended solids (sludge concentration), pH and temperature. Precipitation reactions, which may continue in effluent samples withdrawn for analysis, must be quenched by vacuum filtration and subsequent filtrate acidification to pH, 4.0.

Typical experimental results are illustrated in Figures 7.10 to 7.13, i.e. effect of pH and residence time in Figures 7.10 and 7.11 and the effect of sludge concentration in Figures 7.12 and 7.13.

When sludge recirculation and sludge blanket clarification are utilized in a lime treatment process, which is usually the case, the choice of reactor residence time is not critical, as long as it exceeds approximately 2 minutes (see Chapter 4, Table 4.5). However, when sludge recirculation and sludge blanket clarification are not utilized, as

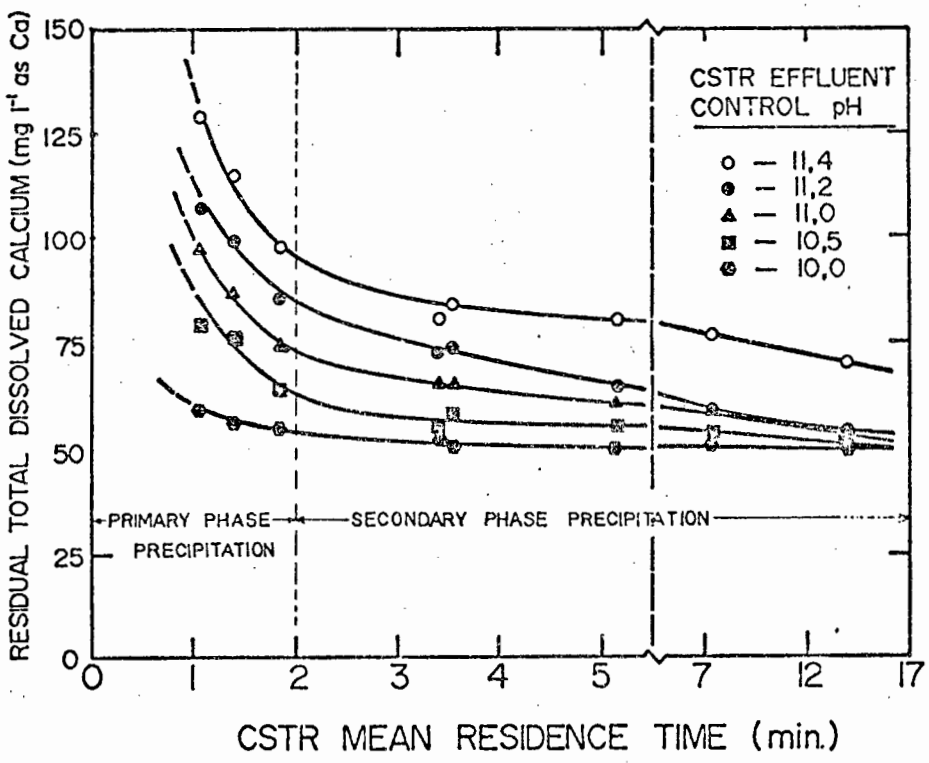

Figure 7.10. Relationship between residual calcium concentration and CSTR residence time for lime-treated secondary effluent in the absence of seed sludge (bench-scale continuous tests)

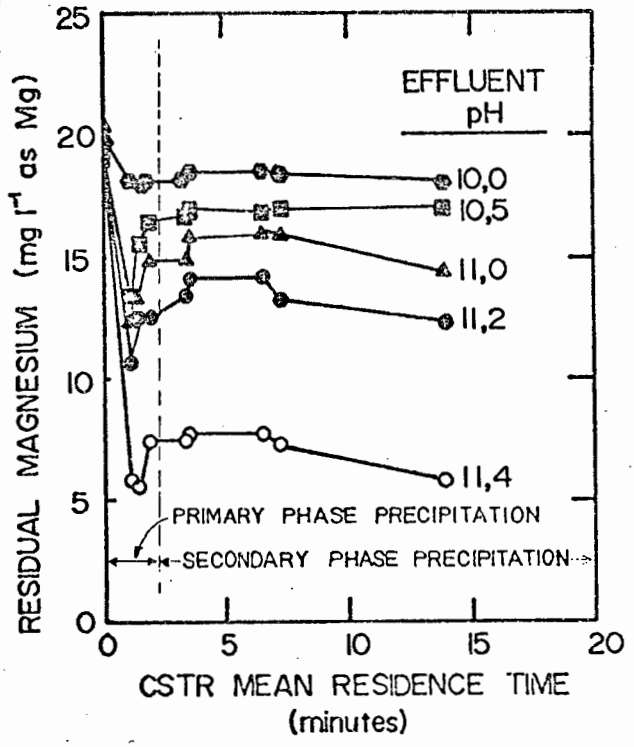

Figure 7.11. Relationship between residual magnesium concentration and CSTR residence time for lime-treated secondary effluent in the absence of seed sludge (bench-scale continuous tests)

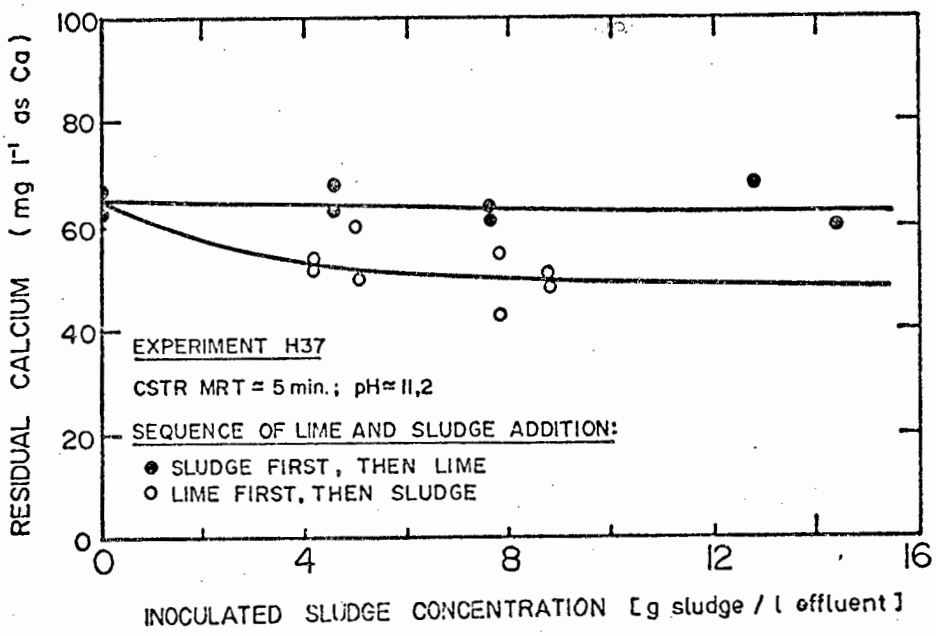

Figure 7.12. Effect of inoculated sludge concentration on residual calcium concentration in CSTR effluent (bench-scale continuous tests)

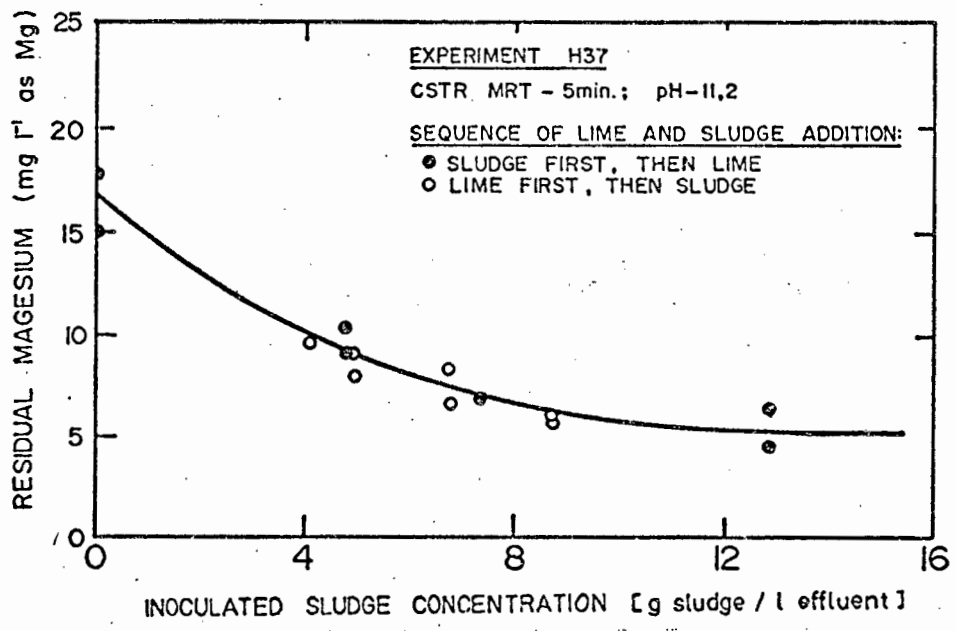

Figure 7.13. Effect of inoculated sludge concentration on residual magnesium concentration in CSTR effluent (bench-scale continuous tests)

in the case of lime treatment of effluent followed by flotation, the reactor residence time prior to flotation is critical. In such cases the mean residence time - residual calcium and magnesium relationships (Figures 7.10 and 7.11) must be used as a basis for selecting the reactor residence time.

Note that no test procedures for flocculation and sedimentation (or flotation) have been given. Clarification tests for the flowrate range at which the bench-scale CSTR tests are usually conducted, e.g. 0,5 to 2,0 $\ell\ min^{-1}$, give information which is not directly applicable to large-scale systems. At these relatively low flow rates clarification (or flotation) units are so small that they do not realistically simulate full-scale plant conditions. Hence clarification tests should preferably be conducted at the pilot scale level, e.g. 0,5 to 5,0 m^3h^{-1}.

3.4 Pilot Plant Investigation

3.4.1 Objectives

Pilot plant tests are usually conducted for the following reasons,

(1) to verify the mean behaviour as determined by bench-scale tests,

(2) to determine the response, stability and variability of the process under the daily and seasonal variations in water temperature and quality,

(3) to investigate flocculation and clarification aspects,

(4) to determine sludge production rates and the effect of *in situ* production of sludge on the precipitation process, and

(5) to formulate control procedures and to establish the stability and practicability of these procedures under varying load conditions.

Before pilot plant tests can proceed a plant must be designed and constructed, based on the information that has been obtained from the batch and bench-scale CSTR tests.

3.4.2 Design and equipment selection

A typical process design lay-out is shown in Figure 7.14.

Influent system

(1) A source of influent to the lime treatment plant must be found. For example, it may be the overflow from a secondary clarifier of a biological treatment plant. Ensure that there will at all times be sufficient influent available at the source to maintain the design influent flowrate, Q_i.

(2) Select a centrifugal pump which has a maximum delivery rate of approximately 1,2x the design influent flowrate. Control over the influent delivery rate is facilitated by operating the pump at a maximum capacity and using a by-pass from the pump delivery side back to the suction side (see Figure 7.14).

(3) Select piping with a diameter, d, which will result in turbulent flow (Reynolds number $N_{RE} > 3,0 \times 10^3$) to ensure that no suspended solids settle out in horizontal sections of piping.

(4) Provide for in-line lime and sludge application points in the influent line prior to the reactor. Select two commercially available static mixers for intense mixing of these two slurries with the influent. The lime application point should always be located upstream of the sludge application point. The application points and static mixers should be positioned in the influent line just ahead of the lime reactor (see Figure 7.14).

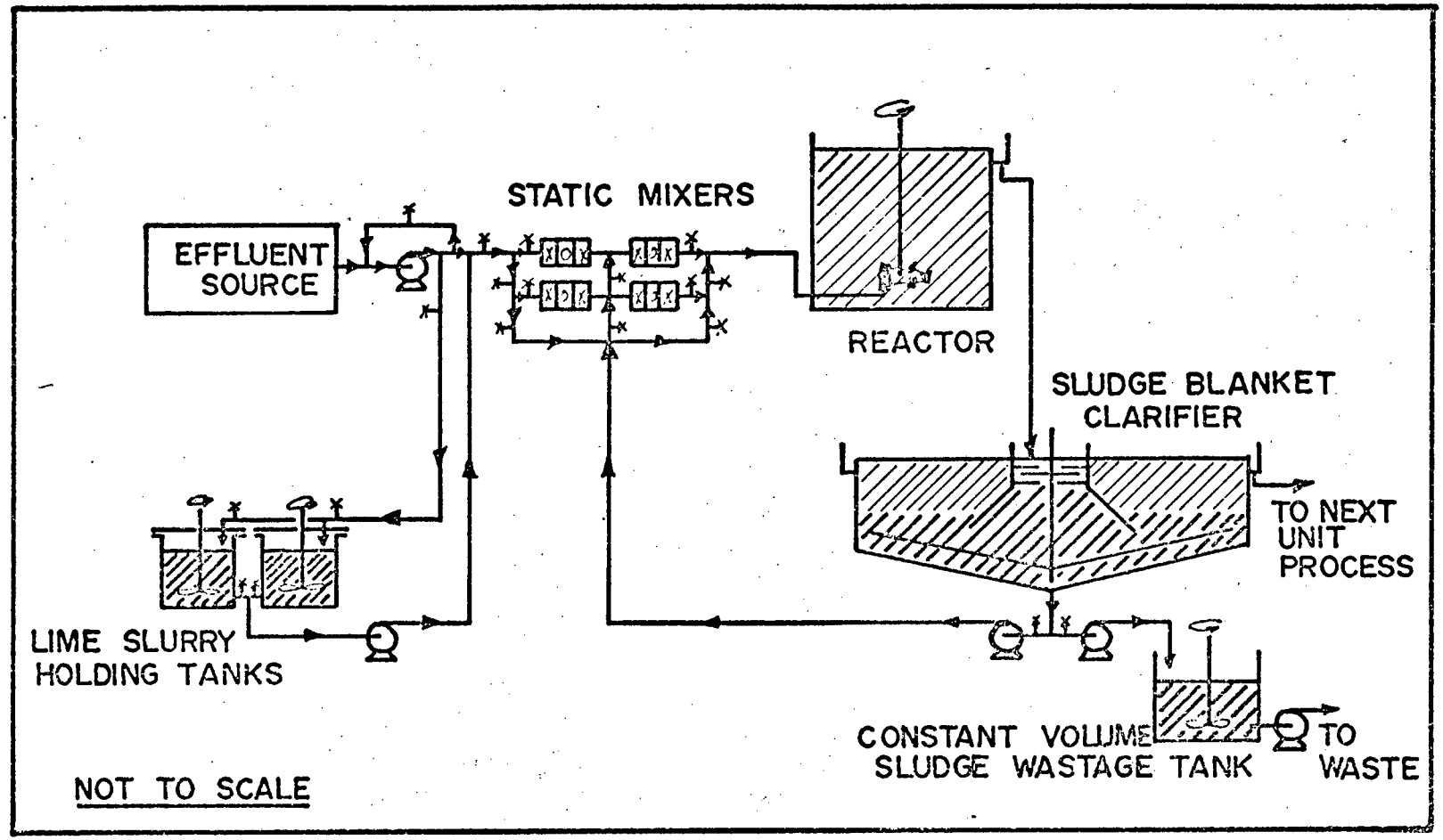

Figure 7.14. Lime treatment process design lay-out (pilot plant)

CSTR system

(1) Decide on a hydraulic retention time, R_H, based on results from the bench-scale studies.

(2) Decide on a convenient reactor flow throughrate, Q_{CSTR}. These are normally in the range 0,5 to 5,0 $m^3 h^{-1}$.

(3) Calculate the CSTR volume, V_c, required to give the selected residence time at the design flow rate.

(4) Design the reactor. Cylindrical mild steel or fibre glass units are most commonly used. Commercially available tanks may be used for this purpose. The radius to water head ratio should preferably be about one. Influent and effluent points must be located as described in the bench-scale CSTR design (Appendix 5). Provision must be made for vertical mixing baffles.

(5) Choose a commercially available stirring device that will give a stirring intensity equivalent to a $\bar{G}$ value of approximate 650 sec^{-1} at a hydraulic retention time of 1 to 5 minutes.

Lime slurry system

(1) Calculate the approximate volume, V_L, of a 2,0 percent lime slurry required over a period of 36 hours to achieve the selected reactor pH value.

(2) Design two lime slurry holding tanks with volume, V_L; vertical baffles as in the CSTR; a draw-off point approximately 5 cm from the bottom of the holding tank; a stirring device to give a $\bar{G}$ value of approximate 650 sec^{-1}; and a cover to minimize slurry-air contact.

(3) Estimate the lime slurry flow rate, Q_L, and select a pump which can deliver lime slurry at flow rates of upto twice Q_L. Care should be taken in the selection of this pump, ensuring that it is suitable for pumping lime slurries. Positive displacement pumps with rubber impeller type drives have been found suitable. Flow rate

selectors with both manual control and electronic interface for closed-loop pH lime dosage control are preferable.

(4) Provide for water to the lime slurry holding tanks. A take-off point from the main influent stream will suffice for this purpose.

Solids removal and sludge system - General

The precipitates formed in the CSTR must be removed from the water by some solid-liquid separation process. Sedimentation, and more recently flotation, have been applied to achieve this objective. There is a considerable body of experience available on settling behaviour (Culp and Culp, 1971), whereas the flotation process has a very recent history in this field (Merrill, 1974; Van Vuuren, Ross and Prinsloo, 1977). It is not the intention to give criteria for the design of these unit processes, but it is pertinent to examine their function in so far as they relate to the precipitation process. Only sedimentation units operating on the sludge blanket clarification principal will be discussed.

A sludge blanket clarifier has various zones (Figure 7.15) which perform specific functions. The effluent from the CSTR system is run into the flocculation zone, zone A. The particles in the reactor effluent are well dispersed throughout the effluent due to the high turbulence in the reactor. The particles aggregate in the flocculation zone due to the presence of the gelatinous $Mg(OH)_2$ flocs and/or added ferricsalts and/or polyelectrolytes. The flocculated mass passes downward and out through the bottom of the flocculation compartment, from where some passes upward into the sludge blanket, zone B, and the balance passes into the sludge thickening zone, zone C, the bottom section of the sludge blanket.

In the sludge blanket zone the upward flow of the liquid and the settling rate of the sludge achieve steady state, manifested by a "blanket" of suspended sludge. The density and depth of the sludge blanket depend on the upward flow velocity of the liquid and the density of the influent suspension. The sludge blanket performs two important functions,

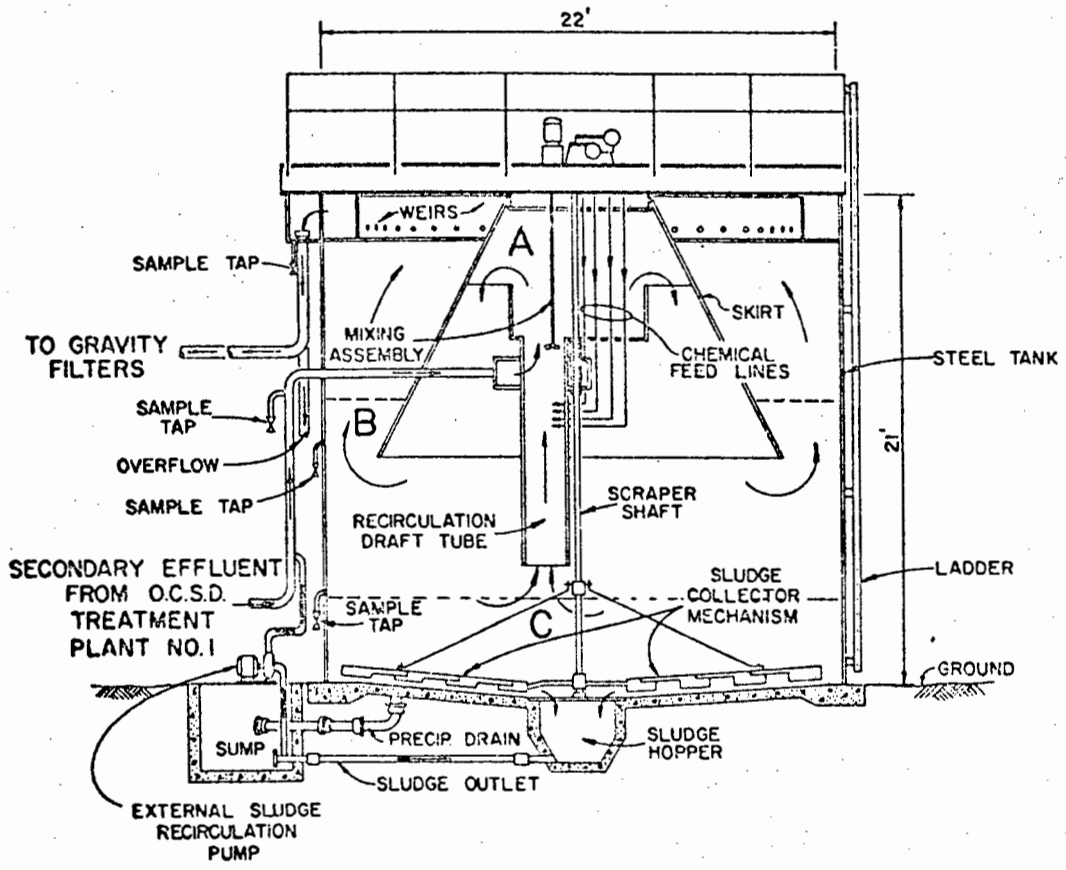

Figure 7.15. Sludge blanket clarifier (After CULP, WESNER, CULP AND BENJES, 1975)

(1) it entraps the fine particles as the liquid passes through the blanket, and

(2) provides further contact opportunity between the supersaturated liquid and the precipitated $CaCO_3$ and $Mg(OH)_2$ solids.

The sludge blanket continuously sheds excess sludge to the quiescent region below the blanket where it is thickened in zone C. The thickened material is moved to the centre of the clarifier by mechanical scrapers where it mixes with the excess flow from the flocculation zone and is withdrawn from the clarifier underflow withdrawal point. The sludge is either returned to the reactor or run into a sludge holding tank for eventual wasting.

The mass of sludge present in the settling tank far exceeds that in the reactor. The steady state sludge concentration in the clarifier underflow is given by the following equation,

$$X_r = X_i \cdot \frac{Q_T}{Q_r} \quad \ldots\ (7.1)$$

Where X_r = steady state sludge concentration in underflow
X_i = steady state sludge concentration in clarifier influent
$Q_T = Q_E + Q_r$ = clarifier influent flowrate
Q_E = clarified effluent flowrate
Q_r = clarifier underflow flowrate

Because of the high fraction of sludge in the clarifier, the rate of underflow recycle has an influence on the sludge concentration in the reactor, the tendency being to increase the fraction of sludge in the reactor as the sludge recirculation rate is increased. This increased sludge withdrawal rate tends to reduce the sludge concentration in the thickening zone (zone C) and also affects the sludge blanket characteristics. Hence a certain measure of control over the sludge blanket is exercised by controlling the sludge recirculation rate.

The mass of sludge in the system, i.e. reactor and clarifier, is determined by the sludge age, R_s. The sludge age is defined as,

$$R_s = \frac{\text{Mass of sludge in the system}}{\text{Mass of sludge wasted per day}} \quad \ldots\ (7.2)$$

and is a measure of the average time the sludge generated by precipitation is retained in the system.

When the plant is started up, no sludge is wasted until the system builds up the desired sludge mass. Thereafter the sludge mass in the system is maintained constant by wasting the same mass of sludge as

that generated per day. Once this steady state has been achieved, the concentration of sludge in the reactor may be altered to a certain extent, by changing the recirculation rate.

In any specific plant the optimum sludge age and recycle rate are affected by the particular clarifier's sludge blanket characteristics Once an optimum operating situation is attained, it should be maintained by some means or other. In many plants this is attempted by maintaining the sludge concentration in the reactor at some constant value, e.g. 10 000 to 15 000 mg ℓ^{-1}. This is achieved by wasting sludge from the clarifier underflow at a rate equivalent to the rate of sludge formation and by manipulating the sludge recirculation rate. However, this method is not very satisfactory since stable conditions are seldom attained.

A simple positive control over the sludge age may be effected as follows : Determine roughly the mass of sludge generated per day; determine the volume of sludge to be removed from the system (by means of wasting clarifier underflow) from the prevailing underflow concentration; remove this volume of sludge to a sludge holding tank (once per day or over the course of a day); waste the sludge from the holding tank to a drain. If the sludge concentration shows an increasing tendency, the volume of sludge wasted should be increased and vice versa. Consequently the sludge holding tank should have a volume providing for 1,5 to 2,0 times the average sludge wastage volume per day.

The form of control described above is relatively simple and easy to execute by operators. It does not lead to extreme fluctuations of the sludge concentration often experienced when control is exercised by the intermittent opening of valves.

Sludge wastage system

Design a system for the removal of a constant volume of sludge. Sludge will be removed once per day or over any other convenient period. Sludge withdrawal from the clarifier underflow will require a pump and a sludge holding tank for collecting and wasting of sludge.

To design the sludge holding tank, calculate the approximate daily solids production rate at the selected control pH from the sludge formed versus pH relationship determined in the batch tests. Assume a sludge concentration of 8 percent and calculate the volume of sludge produced per day, V_s, for the daily flow of secondary effluent to be treated. On this basis design the sludge holding tank to have a volume sufficient to hold the total volume of sludge produce during two days operation, i.e. sludge holding tank volume is equal to $2xV_s$; select a mixing device to give $\bar{G} \simeq 100\ sec^{-1}$, i.e. sufficient turbulence to keep sludge in suspension; make provision for vertical baffles to ensure thorough mixing; and also make provision for withdrawal facilities to a drain. The holding tank must have volume graduations to allow accurate measurement of the sludge volume to be wasted.

Sludge recirculation system

The sludge recirculation system is required to transport sludge from the clarifier underflow to the reactor and to maintain a sludge blanket. The design must be flexible to allow for a range of recirculation rates,

(1) Assume a sludge concentration of approximately 8 percent. Calculate the recirculation rate, Q_s, required to maintain a sludge concentration of 10 000 mg ℓ^{-1} in the reactor.

(2) Select a pump with a maximum delivery rate of approximately twice the estimated maximum recirculation rate. The pump should be of the positive displacement type with a range of pumping rates.

pH control

Various modes of reactor pH control are possible,

(1) *Manual* - Samples are withdrawn and the pH is measured on the plant or in a nearby laboratory. The pH can also be measured directly in the reactor by means of an on-plant pH meter. The lime

dosage is adjusted if necessary, based on this manual pH reading, to correct the reactor pH.

(2) *Automatic* - A closed-loop pH control system is installed to control the lime dosage in such a way that the reactor pH is maintained at a preselected constant pH value. The system comprises a pH detecting device, an interface system to convert the pH signal (millivolts) to a strong electrical signal (volts) which triggers an electronic control system which in turn adjusts the lime slurry pump dosing rate. Various degrees of sophistication are available for such automated systems. A decision will have to be made according to the plant's specific needs. Possibly this decision will only be made after operating the plant manually for some time to establish how critical the need for automation is.

Flocculant aids

It may be necessary to use flocculant-aids to ensure a water with a satisfactory low turbidity from the clarification unit. For this reason provision should be made in the design for the application of two flocculant aids, e.g. ferric chloride and a poly-electrolyte. This will require two holding tanks with mixing devices and two metering pumps.

Once the design has been completed the purchase of equipment and the building of the pilot plant may proceed. Finally, the pilot plant will be commissioned and is then ready for use.

3.4.3 Pilot plant tests

Test procedures

Pilot plant tests procedures are very similar to those for the bench-scale CSTR tests. A test run may be conducted as follows,

(1) Make up all the chemical stock solutions, i.e. lime (5 percent), ferric chloride (10 percent) and polyelectrolyte (1 percent), to last for the duration of the run, i.e. sufficient for at least 24 hours when the next set of chemicals must be made up.

(2) Start-up the plant, i.e. switch on all the paddle stirrers and pumps (influent, lime slurry, ferric chloride, polyelectrolyte).

(3) Set all the flowrates at their selected values (influent, lime slurry, ferric chloride and polyelectrolyte).

(4) Monitor reactor pH regularly and adjust lime dosage, when necessary, to achieve the desired preselected pH value.

(5) Switch on the sludge blanket clarifier scraper arm mechanism and the sludge recirculation pump.

(6) It may require 2 to 4 days to build up the required sludge blanket. Once this has been achieved, sludge should be wasted to a drain at the rate at which it is being produced. A constant volume of sludge must be withdrawn from the clarifier underflow every day (or at regular intervals during the day) into a calibrated sludge holding tank and wasted to a drain from this tank.

(7) Once stable conditions have been established, i.e. a stable reactor pH (fluctuation to within $\pm$ 0,1 of the desired preselected pH value) and stable sludge blanket clarification (blanket level maintained at a constant height - which implies sludge withdrawal more or less at the rate it is produced), water sampling may commence.

(8) The following water samples should be taken :

(a) influent from influent line prior to the lime addition point,

(b) CSTR effluent from the CSTR overflow weir, and

(c) clarifier effluent from the clarifier overflow weir.

These samples may be analysed for :

(a) temperature
(b) turbidity
(c) pH
(d) total alkalinity
(e) total * and dissolved ** calcium
(f) total and dissolved magnesium
(g) total and dissolved ortho- and organic phosphorous
(h) total and dissolved COD
(i) total and dissolved nitrogenous matter (TKN)
(j) total and dissolved solids
(k) ammonia (on filtered sample)
(l) nitrates (on filtered sample)

The frequency of sampling and the degree of completeness of the analysis ((a) to (l) represents a complete analysis) will depend on the purpose of the test.

Mean behaviour

Run a pilot plant test as described above. Verify bench-scale plant results by running pilot plant tests under conditions similar to those studied on the bench-scale plant. If there are significant differences, they will have to be resolved. The differences may be due to the larger scale of operation, the specific process unit configuration used on the pilot plant and the characteristics of the sludge produced *in situ*.

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*"total" refers to analysis on acidified samples where precipitate has been dissolved with HCl; the acidified sample is subsequently filtered (Whatman No. 542) to remove acid insolubles.

**"dissolved" refers to filtered samples (Whatman No. 542); the filtered samples are subsequently acidified to quench any further precipitation reactions.

If the clarified effluent quality does not meet the objectives set for the process, e.g. insufficient magnesium, phosphate or turbidity removal, the operational conditions will have to be altered, i.e. the lime dosage and the sludge concentration may have to be increased and higher flocculant aid dosages may be required. Pilot plant tests for determining the optimum sludge concentration and flocculant aid dosage are described later in this section. Preliminary tests should be conducted at constant sludge and flocculant aid dosages, e.g. 10000 mg ℓ^{-1} sludge, 5 mg ℓ^{-1} $FeCl_3$ (as Fe) and 0,5 mg ℓ^{-1} polyelectrolyte.

Effect of influent daily quality variations

Once a general procedure has been established for achieving stable operation, the effect of influent daily quality variation on the process should be studied. Sewage works effluents are known to display cyclic variations in quality as illustrated in Figure 7.16.

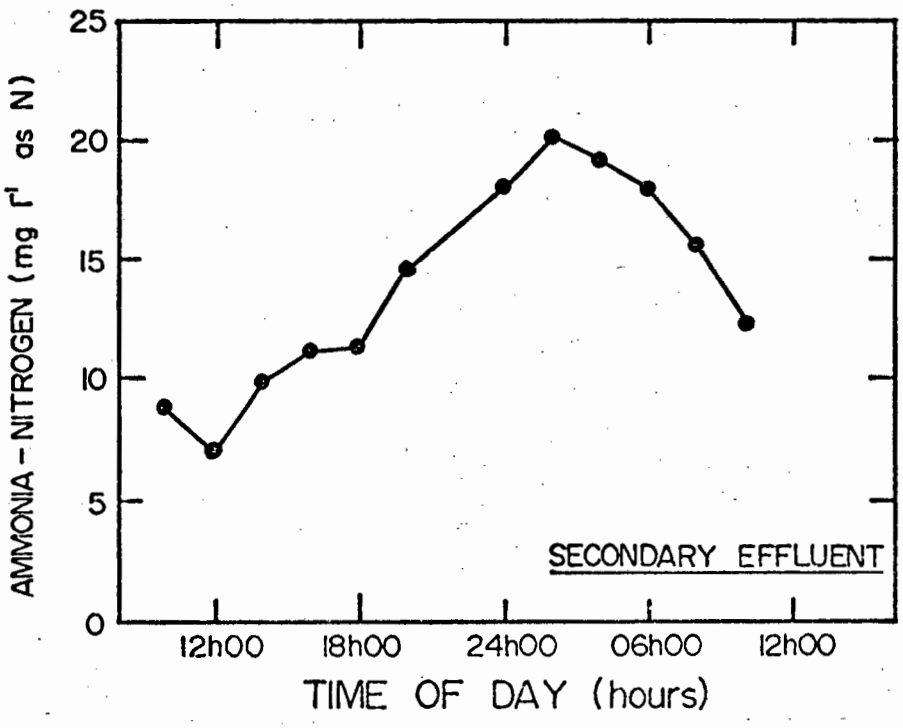

Figure 7.16. Diurnal quality variations in ammonia-nitrogen for secondary effluent from the Pretoria Sewage Works

Operate the pilot plant at constant reactor pH, sludge recirculation rate and flocculant dosage rate. Sample influent and clarifier effluent at two hourly intervals over a period of 36 hours, taking due account of the effect of residence time lags have in the various process units. Analyse these samples for parameters (a) to (l) as listed in the previous section (or less complete, depending on specific objective of the test). Also determine the mean lime dosage over two hour intervals for the total 36 hour test period.

The results will indicate whether the influent quality varies and the effect these variations have on the lime demand and other critical parameters characterizing the effluent. It may be found that with decreasing influent quality, i.e. higher COD, NH_4 and suspended solids concentration, a greater amount of lime is needed to maintain the constant preselected reactor pH. The turbidity of the clarified water may deteriorate, requiring higher flocculant aid dosages or operation at a higher reactor pH. All these aspects should be pursued until a control procedure is established which results in an acceptable effluent under all reasonably expected influent quality variations. These pilot plant tests will establish the system's response, stability and variability under conditions of variable influent quality.

Flocculation and clarification

The need for flocculant aids for the clarification of lime-treated effluent will be indicated by poor turbidity removal results when the pilot plant is run without these chemicals. Should there be a need for flocculant aids all those considered as economically feasible should be screened by the jar test procedure as outlined previously. Once one or more have been selected they should be tested on the pilot plant.

Pilot plant evaluation of flocculant aids should be conducted over a period preferably not less than two to three times the sludge age to allow for stabilization of the flocculant aid concentration in the sludge. Dosage and point of application suggested by the manufacturer

should be considered first. If the results are satisfactory, a cut-back in dosage may be considered. If all the flocculant aids give more or less similar results, they should be evaluated under stress conditions, e.g. reduce the reactor control pH by 0,2 pH units from normal operation to create an effluent which is more difficult to clarify.

A typical test would be conducted as follows : Run the pilot plant until stable conditions are established. Dose flocculant aid continuously to, or just ahead of the flocculation basin in the sludge blanket clarifier. Continue to do this until two sludge age periods have passed. Over a period equivalent to one to two sludge ages monitor reactor pH and clarifier overflow pH, turbidity, total calcium and temperature. After this period change the flocculant aid dosage or change to an alternative flocculant aid. Repeat the above procedure until a satisfactory flocculant aid, both performance and cost wise, is found.

Flocculant aid effectiveness should be interpreted in terms of clarifier overflow quality, making due consideration for influent quality variations. The evaluations are best carried out over long periods to minimize the effects of short period operation under nonrepresentative plant conditions.

Sludge recirculation rate

The presence of sludge in lime-effluent reaction solutions results in significantly improved calcium and magnesium removal. One aspect which has to be evaluated on the pilot plant is the sludge concentration required for optimal precipitation. This may be established by performing a number of pilot test runs at different reactor sludge concentrations, achieved by running at different sludge recirculation rates, e.g. 2, 5, 10, 15 and 20 percent of base flow. Each experiment should be conducted over a period equivalent to 2 to 3 sludge ages to give realistic and comparable results. The parameters which should be monitored are clarifier overflow pH, temperature, residual total alkalinity, residual calcium, magnesium and COD.

The sludge recirculation rate cannot be altered at will, since it affects the sludge blanket clarifier's behavioural pattern. Practical limitations relating to the blanket stability, limit the maximum and minimum sludge recirculation rates. Besides this limitation, care should be taken not to exceed sludge ages of approximately 3 - 6 days, since this may result in partial resolubilization of the COD in the sludge, probably due to hydrolysis of the coagulated COD (Van Vuuren and Wiechers, 1971).

Control procedures

One of the most important aspects which should be studied on the pilot plant is the control procedure necessary for maintaining stable operation. It is a well recognized fact that small treatment plants require a greater degree of control than larger plants and hence the control procedure for a pilot plant will give a conservative estimate of what will be required for a full-scale plant.

(1) *Lime dosage control* - establish on the pilot plant whether lime dosage can be controlled adequately by a manual procedure. The average frequency of pH measurement, with possible associated adjustments in lime dosage rate, to ensure stable operation must be established. Should the manual operation appear very labour intensive and not result in stable operation, automatic control should be considered.

(2) *Flocculant aid dosage control* - Frequency of calibration of the flow rate settings on the pump for accurate dosage must be established. The flow rate often tends to vary with time due to deterioration of the flexible tubing used in these pumps.

(3) *Sludge recirculation rate control* - Frequency of calibration of the flow rate setting on the sludge pump for accurate recirculation rates must be established. Clogging of pumps and connecting pipes and wear and tear on the rubber impeller often take place over a relatively short period (approximately 1 to 3 months), resulting in reductions in flow rate.

Regular checking of the sludge recirculation system is necessary to establish when the system requires cleaning.

(4) *Clarifier control* - This will include control over the sludge blanket height, effluent clarity and sludge wastage rate.

(5) *Water sampling for analysis* - Pilot plant studies over short periods (36 hours) and longer periods (weeks to months), will establish the frequency of sampling required to monitor the lime treatment process adequately.

3.5 Full-Scale Plant Process Design

The laboratory and pilot-scale tests described above may serve as a basis for the process design for full-scale precipitation. Sufficient information may be derived from these tests to ensure a design which will operate efficiently in so far as it affects the precipitation process. Obviously, even though the process design may be efficient, if process unit structural and mechanical configurations are poor, the plant may still not operate satisfactorily. Furthermore, operational optimization will still have to be carried out as identical optimal operational conditions need not necessarily prevail in pilot- and full-scale plants. In all probability the operation and control on a full-scale plant will be easier than on a pilot scale plant, due to the increased influent volumes and equipment size which are controlled by the same highly developed procedures as used on the more fickle pilot plant.

An example of a process design for a full-scale lime treatment plant treating 4,5 Mℓ d^{-1} Pretoria Sewage Works secondary effluent is given below. It was assumed that available finances for this process design would allow for only laboratory batch and bench-scale tests, as may often be the case in practice. Aspects dealt with, are the specified objectives of the treatment, design sequence and process design details for the influent and reactor systems.

3.5.1 Objectives

Assume the following objectives - commonly specified for lime treatment as applied in water reclamation,

(1) ortho-phosphate removal to a residual less than 0,2 mg ℓ^{-1} (as P),

(2) magnesium hardness removal to a residual less than 20 mg ℓ^{-1} (as $CaCO_3$),

(3) 95 percent conversion of ammonium ions to dissolved gaseous ammonia,

(4) minimal sludge generation,

(5) a treated water practically stable with respect to calcium carbonate, i.e. the lime-treated clarifier effluent must not give rise to precipitation of more than 10 mg ℓ^{-1} as $CaCO_3$ on standing for 24 hours,

(6) maximum removal of suspended, colloidal and dissolved organic matter, and

(7) clarifier effluent turbidity less than 2 Jackson Turbidity Units.

3.5.2 Design sequence

(1) Characterization of untreated water - Refer Chapter 7, Section 3.1 (Also see Chapter 4, Section 2.1, Table 4.2)

(2) Predict effluent response to lime treatment using a Modified Caldwell-Lawrence Diagram - Refer Figures 7.1 to 7.5 (Also see Chapter 4, Section 5.2).

(3) Laboratory batch tests - Refer Figures 7.1 to 7.5 (also see Chapter 4, Sections 3 and 5).

(4) Bench scale CSTR tests - Refer Chapter 4, Section 4.

(5) Process design for full-scale plant - Will be based on information gathered in (1) to (4) above, as further discussed in the next two subsections.

3.5.3 Preliminary considerations

The attainment of a number of the objectives listed in Section 3.5.1 are coupled to reaction pH. A decision regarding the necessary reaction pH can be made on the basis of the batch and bench scale CSTR test results (refer Chapter 4, Sections 3, 4 and 5),

(1) A pH in excess of 10,5 is required for achieving an ortho-phosphate residual less than 0,2 mg ℓ^{-1} (as P).

(2) A pH in excess of 11,2 is required for achieving a magnesium residual less than 20 mg ℓ^{-1} (as $CaCO_3$). In addition a sludge concentration of approximately 10,0 g ℓ^{-1} is necessary to achieve this magnesium residual at pH 11,2.

(3) A pH of approximately 10,8 (at 20°C), is required for 95 percent conversion of ammonium ions to ammonia (see Figure 7.17).

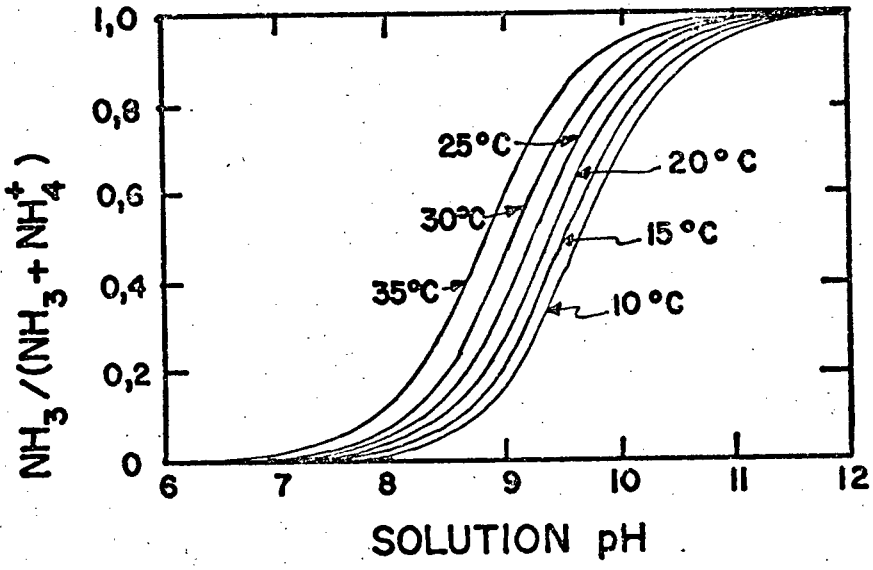

Figure 7.17. The effect of pH and temperature on the distribution of the NH_4^+ and NH_3 forms of ammonia-nitrogen (After SRINATH and LOEHR, 1974)

Objective (2) determines the minimum pH which is required to attain objectives (1) to (3). Operation at pH values in excess of 11,2 will also result in the attainment of objectives (1) to (3), but will be contrary to objective (4). The reactor effluent control pH is therefore chosen to be 11,2 in accordance with objective (4). At this pH value the lime dosage will be approximately 350 mg ℓ^{-1} (as lime) and sludge production approximately 470 mg ℓ^{-1} (see Chapter 4, Tables 4.11 and 4.12).

Objective (5) requires a lime-effluent reactor vessel with a minimum hydraulic retention time of 2 minutes, sludge recirculation to this vessel to result in a sludge concentration of not less than 10 g ℓ^{-1} and a sludge blanket clarifier to produce sludge of the necessary concentration (see Chapter 4, Section 4.3, Figure 4.14).

The attainment of objectives (6) and (7) is closely related to the design and operation of the solid-liquid separation process. Depending on the efficiency of the sludge blanket clarifier, flocculant aids such as ferric chloride and polyelectrolyte may or may not be required to assist in attaining these objectives. Realistic evaluation of this aspect can best be made on the full-scale plant when it is operational.

3.5.4 Process design

Influent system

(1) *Influent source* - Pretoria Sewage Works secondary effluent. This secondary effluent is drawn from the works secondary clarifier overflow collection sump.

(2) *Base flow* - 4,5 Mℓ d^{-1}. The sewage works produces between 10 and 35 megalitre secondary effluent per day and hence there should always be sufficient effluent from this source and storage is not necessary.

(3) *Influent pump* - select a centrifugal pump with a minimum capacity of 1,2x the desired influent flow rate, Q_i (= 4,5 Mℓ d^{-1}), i.e. Q_i^1 = 5,5 Mℓ d^{-1}. The flow may be throttled back with one valve, or alternatively with two valves and a by-pass system from the delivery to the suction side of the pump.

(4) *Pipes transporting influent to the lime treatment plant* - Select a pipe diameter which will result in turbulent flow to ensure that suspended solids do not settle out in horizontal sections of the pipeline. For a base flow of 4,5 Mℓ d^{-1} a pipe diameter of 19,6 cm (standard 8 inch pipe) will give the required turbulent flow.

(5) *Static mixers and lime and sludge application points* - Select two commercially available six segment static mixers. Their diameters should be compatible with the standard pipe diameter selected for the influent system, i.e. 19,6 cm. The position of the static mixers and the lime and sludge slurry application points in the influent line are shown in Figure 7.14. It is recommended that a duplicate system and/or a by-pass system is allowed for in the design for periods when the normal on-line system has to be dismantled for descaling. The frequency of descaling is estimated at approximately three monthly intervals.

Reactor system

(1) Hydraulic retention time, R_H = 2 min.

(2) Flow-through rate,

$$Q_{Reactor} = Q_{influent} + Q_{lime\ slurry} + Q_{sludge\ slurry}$$
$$= 3125 + 55 + 313$$
$$= 3493\ \ell\ min^{-1}$$

($Q_{lime\ slurry}$ and $Q_{sludge\ slurry}$ calculations are given below)

(3) Reactor solution volume = $R_H \times Q_{reactor}$ = 3493 x 2,0 = 7,0m^3.

(4) Reactor radius (R) to water head (H) ratio must preferably be 1:1, H = R = 1,3 m to ensure minimum area for scale formation. However, mixing considerations may dictate a different geometric design.

(5) Select a commercial stirring device that will give a $\bar{G}$ value of approximately 650 sec^{-1}.

Lime slurry system

(1) Calculate daily lime consumption,

$$LC = LD \times Q_i$$
$$= 350 \times 4,5 \times 10^6 \times (10^{-6} \text{ kg/mg})$$
$$= 1575 \text{ kg } d^{-1}$$

where LC = Daily lime consumption (kg d^{-1})
LD = Effluent lime demand (mg ℓ^{-1})

The application of such large quantities of lime is a problem outside the scope of this thesis. Many commercially developed systems are available. The problem reduces to the selection of the system most suitable to the specific plant.

(2) Lime slurry flow rate,

$$Q_i = LD \times Q_L/LS$$
$$= 350 \times 4,5 \times 10^6 / (20\,000 \times 24 \times 60)$$
$$= 55\ell \text{ min}^{-1}$$

where Q_L = lime slurry flow rate (ℓ min^{-1})
LS = lime slurry concentration (mg ℓ^{-1})

Select a commercially available pump which can pump a 2 percent lime slurry at variable pumping rates in a range of approximately zero to $2Q_i$.

Sludge system

The design of a sludge blanket clarifier or guidelines for the selection of commercially available units are outside the scope of this thesis. The reader is referred to the literature for this purpose (see Section 3.4.2).

In the design of the sludge recirculation system provision must be made for a sludge recirculation pump that can pump a 5-10 percent sludge (M/V) at a rate of approximately 10 percent of base flow, i.e. 313ℓ min^{-1}. Select a commercially available pump for this purpose which has a maximum delivery rate of $2Q_s$ with pumping rates in the range of of approximately 0-600ℓ min^{-1}.

The above comprise the basics necessary for the process design of a lime treatment reaction system.

4. RECARBONATION

Lime treatment of secondary effluent for the purpose of reclamation results in a water with a relatively high pH, e.g. 11,0 to 11,6. This high pH water may be passed through an ammonia stripping tower for ammonia removal, in which case the pH will drop to, e.g. between 10,8 to 11,4. Effluents with such high pH values are not suitable for treatment in subsequent reclamation unit processes, such as chlorination and carbon adsorption. Even if chlorination and carbon adsorption are not required, the high pH effluent cannot be discharged into a reticulation system because any contact with air will result in CO_2 absorption and subsequent $CaCO_3$ precipitation. The secondary effects of CO_2 absorption and $CaCO_3$ scale formation are considered in Section 5.

The high pH of the lime-treated effluent may be reduced by recarbonation. In the recarbonation process carbon dioxide is added to the lime-treated effluent to reduce its pH to an acceptable level for discharge to reticulation systems, i.e. a pH which corresponds to a saturated (with respect to calcite) water - usually in the range 8,0 to 9,0 - this is referred to as single stage recarbonation. The effluent may in some instances also be partially softened by means of the recarbonation process - this is referred to as the two-stage recarbonation process. In such a process the pH is first reduced to a value of, e.g. 9,8 to 10,4, to create a water with zero Acidity - which corresponds to the condition required for optimal softening (see later). After a phase separation step for removal of precipitated calcium carbonate, the softened water is stabilized by reducing the pH to a value, e.g. 7,5 to 8,5, consistent with conditions for a water saturated with respect to calcite.

The fundamentals of the recarbonation process have been adequately described in the literature (Loewenthal and Marais, 1976; Manual for water reclamation, NIWR, 1977). The recarbonation system described by Loewenthal and Marais (1976) is applicable in cases where true solid-liquid phase calcite equilibrium states are attained. As was demonstrated in Chapter 6, calcite equilibrium is not attained in the recarbonation-softening process as applied to lime-treated secondary effluent, but the equilibrium model is still valid if a different calcium carbonate solubility product value is used, i.e. $pK_{CaCO_3} = 10^{-7,1}$. A Modified Caldwell-Lawrence Diagram with this solubility product has been constructed and hence predictions for softening by recarbonation should be made using this specific Diagram.

Example 1

Soften an ammonia stripping tower effluent which has the following constitution,

pH - 11,49
Total Alkalinity - 190 mg ℓ^{-1} (as $CaCO_3$) ≡ 3,80 mmol ℓ^{-1}
Calcium Hardness - 190 mg ℓ^{-1} (as $CaCO_3$) ≡ 1,90 mmol ℓ^{-1}
Ionic strength - 0,0125
Temperature - 23°C

Select a Modified Caldwell-Lawrence Diagram applicable to the problem under consideration, i.e. $pK_{CaCO_3} = 7,10$, temperature = 20°C, $\mu = 0,015$ and $Mg_T^{2+} = 0,00$. Draw in the constant parameter lines for pH, Alkalinity and calcium, as shown in Figure 7.18. The intersection of the Alkalinity and calcium lines (point A) defines the parameter "$Alk-2Ca_T^{2+}$" which is equal to zero. The intersection of the pH and Alkalinity lines (point D) defines the Acidity of the solution, i.e. equal to -2,50 mmol ℓ^{-1}. To optimally soften this water by recarbonation requires CO_2 addition sufficient to attain a point E in Figure 7.18, i.e. sufficient CO_2 to change the effluent Acidity from -2,50 mmol ℓ^{-1} to zero (from point D to point E). The quantity of CO_2 required for this purpose is 2,50 mmol ℓ^{-1} CO_2 ($=Acid_D - Acid_E$) and the quality of the resulting softened water will be,

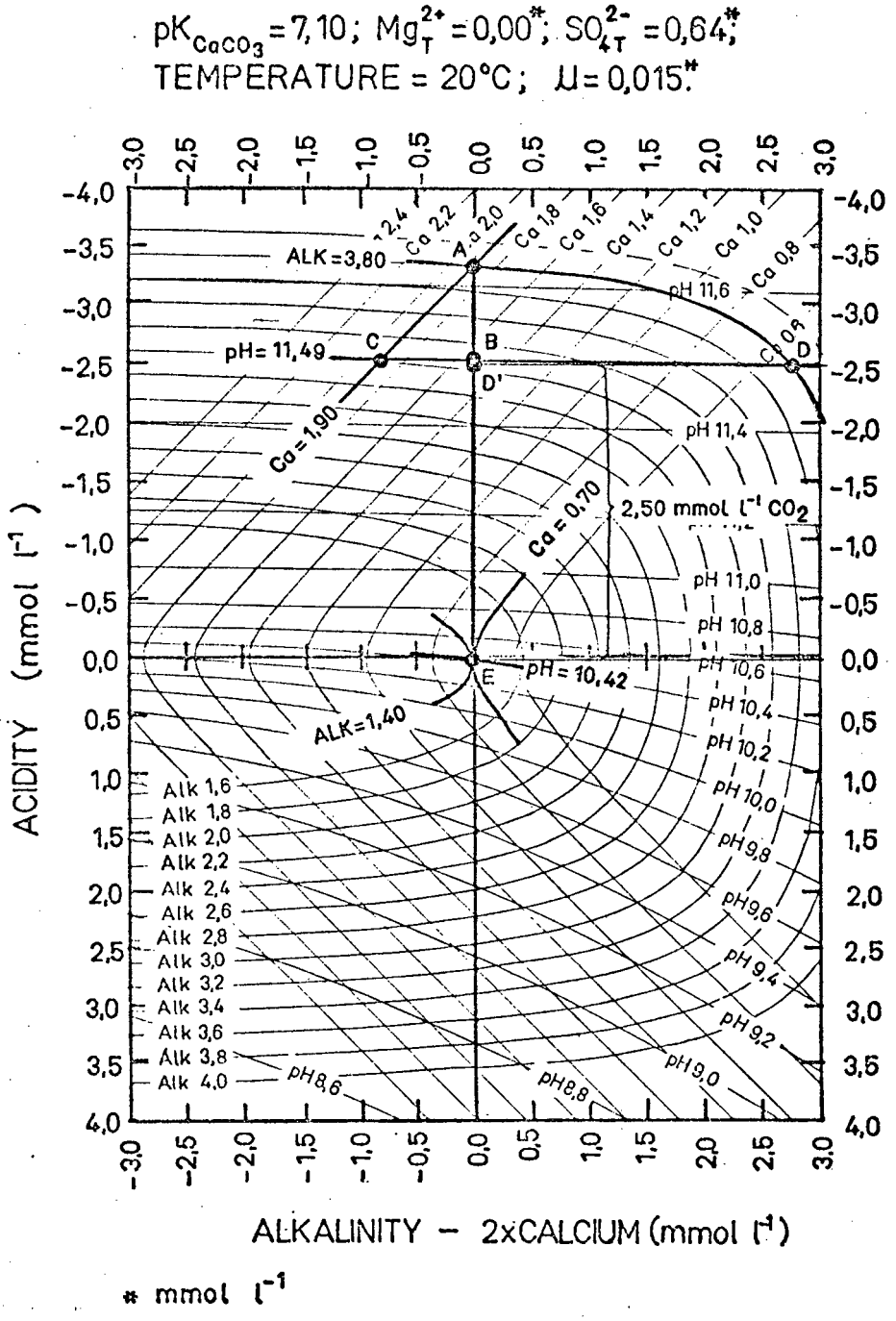

Figure 7.18. Plot demonstrating the use of the Modified Caldwell-Lawrence Diagram (pK$_{CaCO_3}$ = 7,10) for recarbonation - softening predictions

pH - 10,43
Total alkalinity - 1,40 mmol ℓ^{-1} ≡ 70 mg ℓ^{-1} as $CaCO_3$
Calcium Hardness - 0,70 mmol ℓ^{-1} ≡ 70 mg ℓ^{-1} as $CaCO_3$
Hardness precipitated - 130 mg ℓ^{-1} (as $CaCO_3$)

At present no exact knowledge exists on the solubility of the $CaCO_3$ in the final reclaimed water. It is possible that the processes of chlorination and carbon adsorption normally encountered in a train of reclamation unit processes may again change the solubility of calcium carbonate in the final effluent, i.e. through the destruction or removal of heterogeneous substances inhibiting calcium carbonate precipitation. It is the objective of water stabilization processes to produce a water which will be stable, i.e. a final effluent which will not cause scale formation but on the other hand should also be non-corrosive. Due to the lack of knowledge on pK_{CaCO_3} values for final reclaimed water it is recommended that the classical thermodynamic value for the calcite solubility product, i.e. pK_{CaCO_3} = 8,35 (at 20°C) be used as a criterion for stabilization.

Example 2

Stabilize the softened effluent produced in the Example 1. First select a Diagram suitable to the problem under consideration, i.e. pK_{CaCO_3} = 8,35, temperature = 20°C, μ = 0,015 and Mg_T^{2+} = 0,0. Draw in constant parameter lines for pH, Alkalinity and calcium as shown in Figure 7.19. From this Diagram it appears that the effluent is oversaturated. In order to stabilize this effluent CO_2 must be added to change the effluent Acidity from zero (D and D') to 1,40 mmol ℓ^{-1} (point E), i.e. the effluent quality (Alk = 1,40 and Ca_T^{2+} = 0,70 mol ℓ^{-1}) at which this effluent is in equilibrium with respect to calcium carbonate. Stabilization is achieved by reducing the pH of the effluent from pH = 10,42 to 8,32 using carbon dioxide.

The above two examples illustrate typical calculations for a two-stage recarbonation process. In a single stage recarbonation process no intermediate softening is attempted by the addition of carbon dioxide. The quantity of CO_2 added to the lime-treated water is sufficient to stabilize it. The procedure for calculating the quantity of CO_2 required for single-stage recarbonation-stabilization is identical to

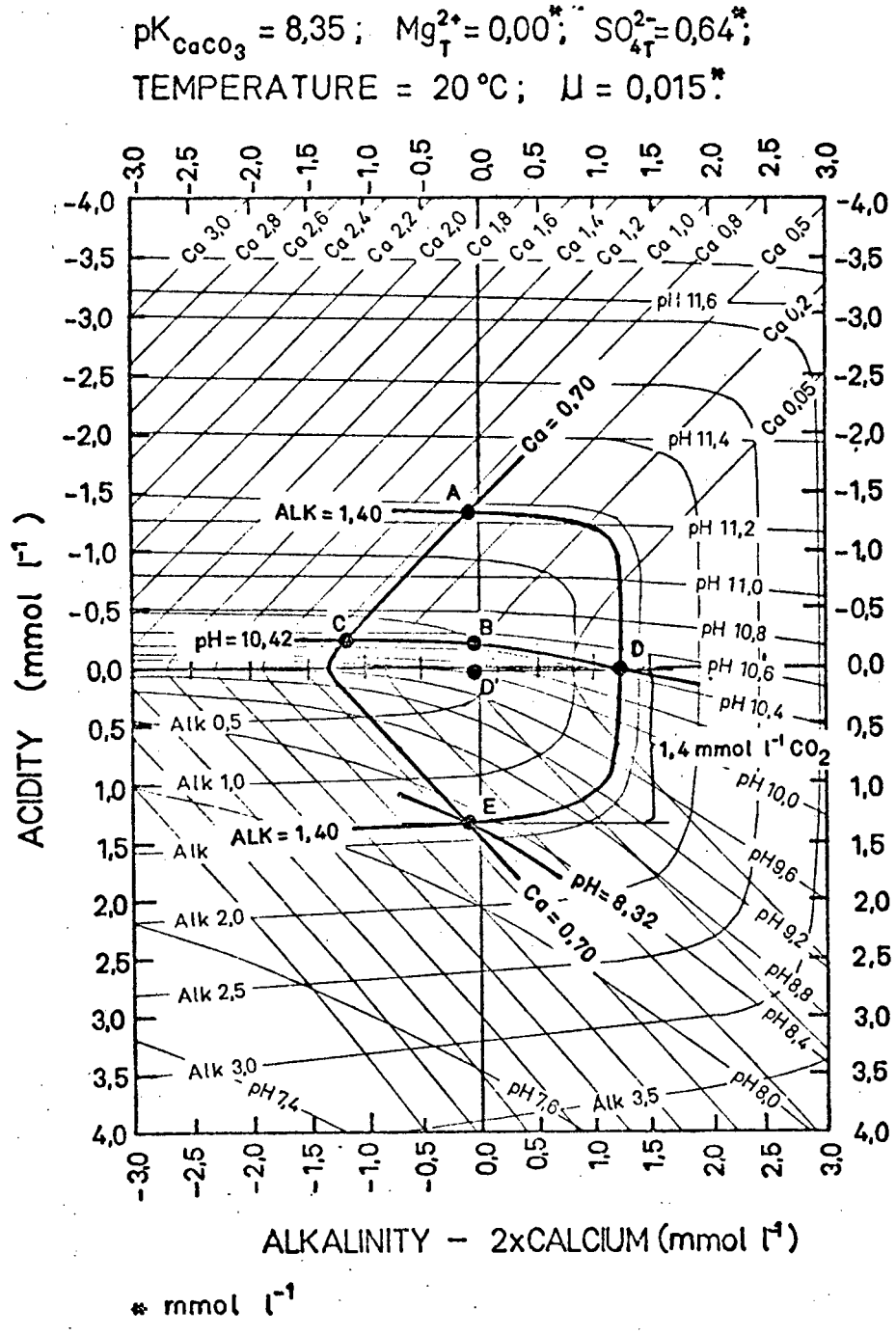

Figure 7.19. Plot demonstrating the use of the Modified Caldwell-Lawrence Diagram (pK_{CaCO_3} = 8,35) for final effluent stabilization predictions.

the procedure used in Example 2.

5. SCALE FORMATION

One of the most troublesome problems associated with lime treatment, as applied in water reclamation, is calcium carbonate scale formation. Both soft and hard scales may usually be noted on equipment in contact with lime-treated water, i.e. clarifier weirs and troughs, pipelines, pumps and sumps. As discussed in Chapter 5, Section 5.2 , this scale formation is primarily due to absorption of carbon dioxide from air in contact with the high pH lime-treated water. Reaction of the absorbed carbon dioxide with the alkaline effluent results in a solution supersaturated with respect to calcium carbonate. Precipitation follows, usually in the form of scale formation on equipment surfaces in contact with the supersaturated solution. Because the degree of supersaturation is very slight, the rate of precipitation is relatively slow and may take place over considerable lengths of piping.

Three specific problem areas on the Stander Plant are discussed, i.e.

(1) Primary clarifier weir, trough, sump and pipe connecting the trough and sump.

(2) Clarifier sump pump and connecting piping to and from the equalization basin.

(3) Ammonia stripping tower sump pump and pipe to recarbonation reactor.

5.1 Primary Clarifier Weir, Trough, Sump and Pipe Connecting Trough and Sump

Under free-fall conditions over the primary clarifier weir lime-treated effluent absorbs carbon dioxide, causing soft scale deposits on the weir and in the collection trough and hard scale formation in the pipe connecting the trough with the clarifier sump and also in the sump. The soft scale deposits on the weir and in

the collection trough do not pose a big problem as this is controlled by daily brushing. The deposits in the sump are also of little consequence due to the relatively large volume of the sump. However, the scaling problem in the connecting pipe between the collection trough and the sump is very severe, i.e. a 50 mm thick scale layer formed in this pipe over a period of about two years. This resulted in a flow reduction of about 50 percent (within a period of 2-3 months), and required an unscheduled plant shutdown for descaling.

To overcome the problems associated with scale formation for this specific problem area, two modifications to the present clarifier weir and sump design are suggested (also see Chapter 5, Section 5.2), i.e.

(1) Covers to the overflow weir should be provided to reduce effluent contact with the air. A possible design is shown in Figure 7.20. The problem could also be minimized if the sump is built contiguous to the clarifier so that no pipe connection is necessary (Figure 7.21). The construction must be such as to allow easy access for mechanical descaling (should this be necessary),

(2) The pipe connecting the clarifier trough and sump should be replaced by an open duct. A gravity flow system should replace the pump system, if at all possible.

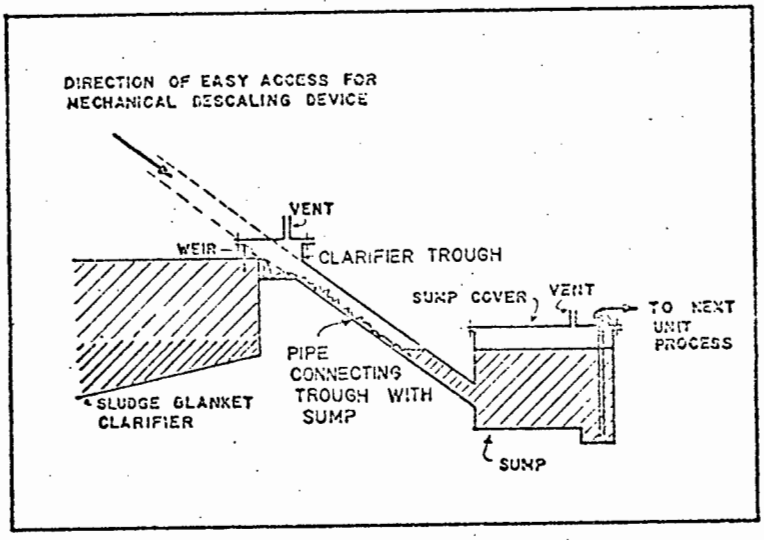

Figure 7.20. Suggested design for an accessible pipe connecting the clarifier trough and sump

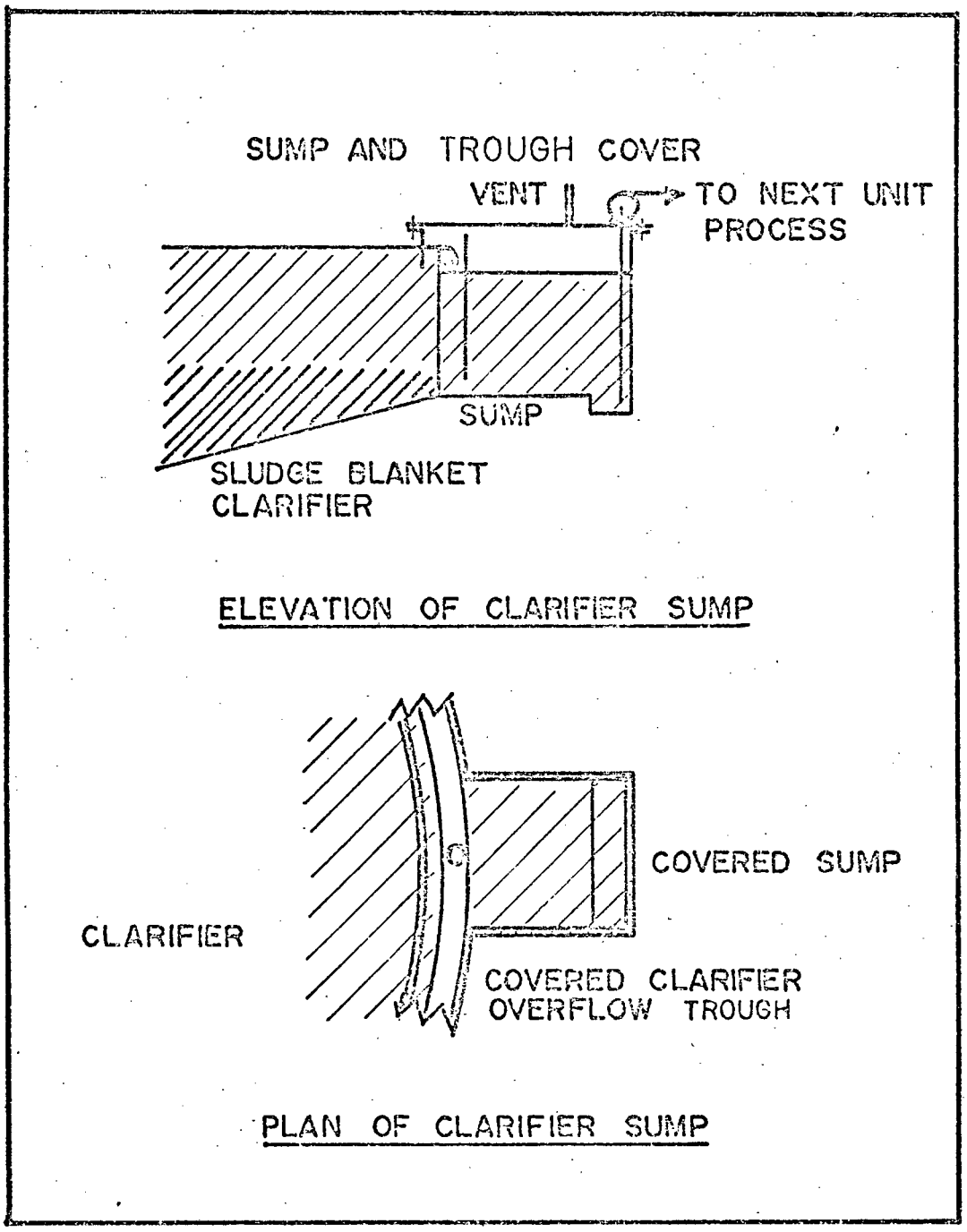

Figure 7.21. Suggested design for sump contiguous to the clarifier

5.2 Clarifier Sump Pump and Connecting Piping to and from the Equalization Basin

Severe scaling has been observed in the clarifier effluent sump pump, which pumps effluent to the equalization basin, and in the connecting piping to and from the equalization basin. This problem will most probably be reduced when design recommendations given in Section 5.1 above are implemented. To minimize maintenance problems, the connecting piping should be positioned such that sections can be easily removed for cleaning or so that it is possible to clean the pipe *in situ*.

Moderate scaling was observed in the pipe connecting the equalization pond overflow to the pond overflow sump. Again a cover over the overflow weir similar to that proposed for the primary clarifier should minimize this problem. Site selection to provide for gravity flow will obviously greatly minimize the problem, since a pump would not be required and open ducts could be used.

5.3 Ammonia Stripping Tower Sump Pump and Pipe to Recarbonation Reactor

Severe scaling was observed in the ammonia stripping tower effluent sump pump. During continuous operation this pump had to be stopped at 2 to 3 month intervals for maintenance to remove scale, since it could not maintain plant flow. Severe scaling was also observed in the pipe from the sump to the recarbonation reactor. Scale formation is mainly attributed to carbon dioxide absorption in the ammonia stripping tower resulting in an effluent which was supersaturated with respect to $CaCO_3$.

Two solutions are suggested depending on whether two-stage or single stage recarbonation is practiced.

Two stage recarbonation

Sludge from the secondary clarifier is recycled into the ammonia stripping tower effluent sump (see Figure 7.22). The sludge is kept in suspension in the sump by mechanical stirring. The mixture is pumped from the sump to the recarbonation reactor. Carbon dioxide for recarbonation is added in-line just ahead of the recarbonation reactor

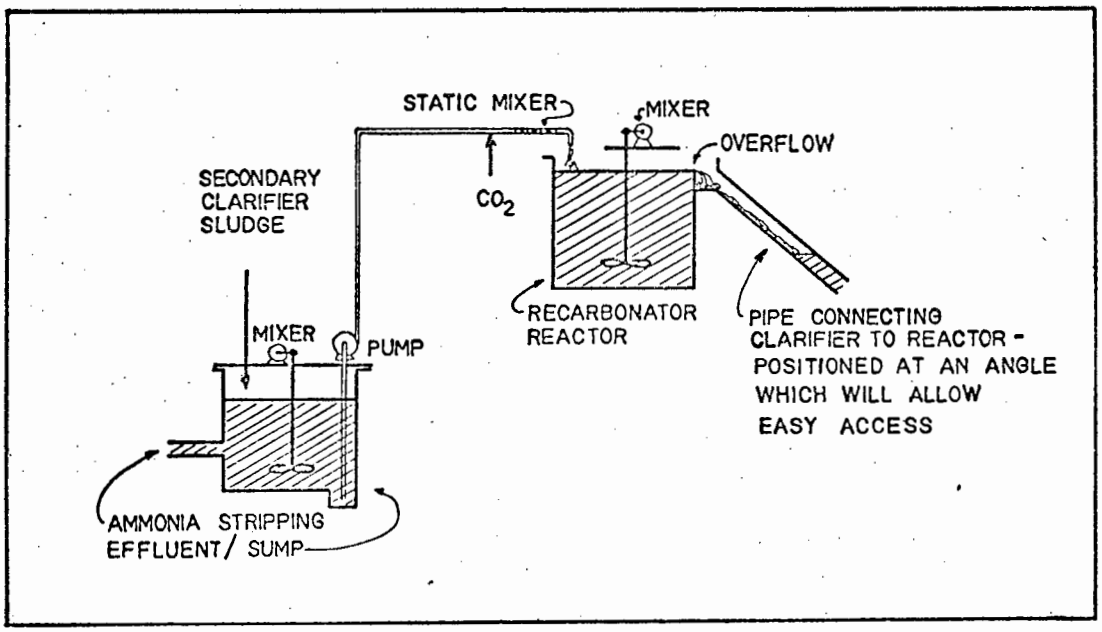

Figure 7.22. Suggested design for first-stage recarbonation system

and is thoroughly mixed with the solution by means of a static mixer. The high concentration of crystal seed mass (sludge) will promote precipitation of $CaCO_3$ from the supersaturated ammonia stripping tower effluent onto the sludge, thereby reducing the scale formation on the pump and transporting piping.

Single stage recarbonation

Carbon dioxide is added to the effluent to achieve a pH at which no $CaCO_3$ will precipitate. Consequently no sludge will form which can be recycled to the ammonia stripping tower effluent sump. Scaling in the ammonia stripping tower sump pump and pipeline to recarbonator reactor can possibly be prevented or reduced, by feeding the small quantities of carbon dioxide, which have to be applied for stabilization, into the intake of the induction pipe to the pump. The turbulence in the pipe and pump should be sufficient to cause complete dissolution of

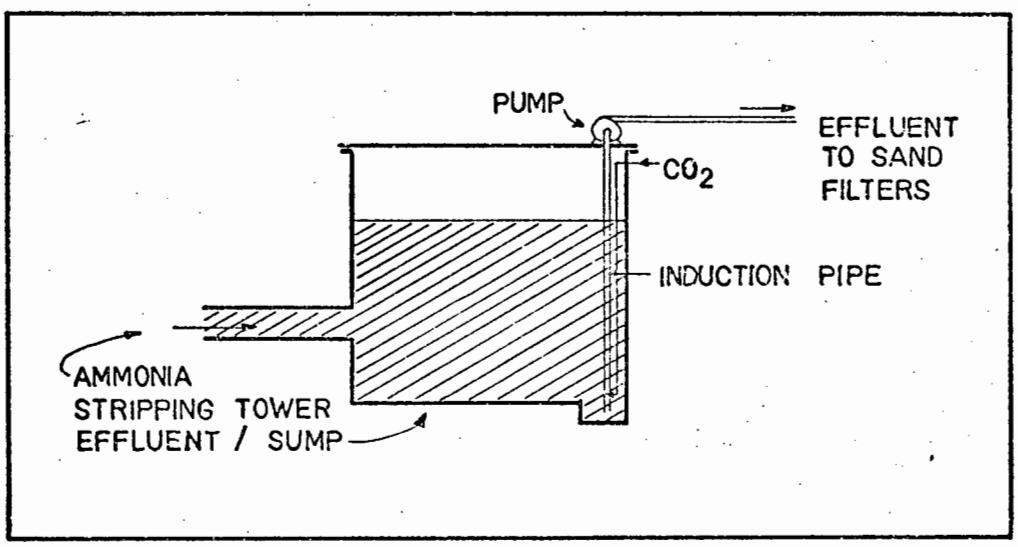

Figure 7.23. Suggested design for single-stage recarbonation system

the carbon dioxide. Should experience indicate that this mode of dissolution is inadequate or result in pump corrosion, a static mixer could be inserted in the induction pipe to the pump (see Figure 7.23).

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CHAPTER 8

GENERAL CONCLUSIONS

The thesis has dealt in depth with the engineering aspects of calcium carbonate and magnesium hydroxide precipitation in waste water reclamation. In this study both the fundamental and empirical approaches were used. The fundamental approach yielded insight into the essence of the precipitation kinetics and equilibria associated with the $CaCO_3$ and $Mg(OH)_2$ systems. However, due to the extreme complexity of precipitation processes in heterogeneous systems, the fundamental approach was abandoned for the empirical approach which yielded practical solutions to the problems of reactor design, post precipitation and scale formation associated with the lime and recarbonation processes.

Calcium carbonate precipitation in pure synthetic solution systems, simulating lime treatment and recarbonation process conditions - high degree of supersaturation, high pH and high seed mass, is adequately modelled by the rate equation proposed by Sturrock, Benjamin, Loewenthal and Marais (1976),

$$\frac{\delta[CaCO_3]}{\delta t} = k_G.CaCO_3(s).f_D.\{[Ca^{2+}]^{\frac{1}{2}}[CO_3^{2-}]^{\frac{1}{2}} - (\frac{K_{sp}}{f_D^2})^{\frac{1}{2}}\} \quad .... \quad (8.1)$$

The effects of temperature, seed crystal concentration and stirring speed have been isolated and quantified. The mechanism of $CaCO_3$ crystal growth is one of surface controlled growth. Unfortunately the rate constants for $CaCO_3$ crystal growth, k_G, differ by as much as a factor of five for seed crystals of different origins, limiting the practical application of Eq. (8.1).

An empirical study of $CaCO_3$ and $Mg(OH)_2$ precipitation in lime-treated effluents confirmed that the kinetics of precipitation are not crucial to the final effluent quality if the following reaction conditions are adhered to,

(1) Lime slurry and sludge, in that order, are thoroughly mixed, preferable by means of in-line static mixers, with the raw water before discharge to a CSTR.

(2) A CSTR with a minimum mean residence time of 2 minutes is supplied for the chemical dissolution and precipitation reactions to go to completion.

(3) The reactor contents have a sludge concentration of the order of 10 000 mg ℓ^{-1}.

Effluent from such a reaction system shows no significant post-precipitation.

Optimum results on the full-scale Stander Reclamation Plant are achieved when operating the lime treatment process in a mode where a CSTR reactor is used prior to a sludge-blanket clarifier and the sludge from the clarifier underflow is recirculated up-stream of this reactor.

Long term scaling effects result due to carbon dioxide absorption by saturated lime-treated secondary effluent at clarifier weirs and troughs. It is therefore essential in the design of a lime treatment process to minimize effluent-air contact opportunity. In addition, some scale formation on surfaces in contact with lime-treated effluent is inevitable in the long term, and design must be such that all surfaces and specifically transporting systems, are accessible for mechanical cleaning.

The quality of the lime-treated secondary effluent, the lime demand and the sludge generation rate are adequately predicted by means of an equilibrium model based on $pK_{CaCO_3} = 6,7$ and $pK_{Mg(OH)_2} = 10,5$. The quality of recarbonated effluent is adequately predicted by the equilibrium model based on $pK_{CaCO_3} = 7,1$.

Although the two constants for lime-treated secondary effluent were developed for effluent from the Stander Plant, they also give good predictions for lime treated-secondary effluents of widely different origins, thereby indicating the broad application of the model and its potential

as a generalized model. The practical value of the new model and its associated graphical technique is evident when comparing model predictions with predictions based on the pK values for calcite and brucite, i.e. an improvement of upto 80% in prediction accuracy is observed.

All the fundamental and empirical data of apparent practical value collected during this study are condensed in the form of process design guidelines. Whether these guidelines will in fact be practical, e.g. as in the case of the suggested covers over clarifier weirs, troughs and sumps, is at present a matter for speculation. Similarly, the suggested "ideal" design sequence may prove unnecessarily detailed. Thus, although it is anticipated that the suggested design guidelines will result in improved precipitation process designs, only success in the practical application of these guidelines will substantiate these expectations.

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APPENDIX 1

PROCEDURE FOR PREDICTING CHANGES IN EFFLUENT CHARACTERISTICS AS A RESULT OF LIME TREATMENT - USING THE MODIFIED CALDWELL-LAWRENCE DIAGRAM *

Detailed procedures for the use and application of the Modified Caldwell-Lawrence Diagram are given by Loewenthal and Marais (1976) in their book "Carbonate Chemistry of Aquatic Systems - Theory and Practice". Two types of Diagrams are dealt with in this thesis,

(1) Diagrams which do not incorporate ion pairing effects. The input data required for this type of Diagram are : *Constants* - temperature and ionic strength; *Variables* - calcium, Alkalinity and magnesium concentrations and pH. The units used for all the parameters except pH are mg ℓ^{-1} (as $CaCO_3$). These Diagrams are applicable to waters where ion-pairing is not significant, such as low ionic strength surface waters.

(2) Diagrams which incorporate ion pairing effects, i.e. for ion pairs $CaOH^+$, $CaCO_3^o$, $CaHCO_3^+$, $CaSO_4^o$, $MgOH^+$, $MgCO_3^o$, $MgHCO_3^+$, $MgSO_4^o$, $NaSO_4^-$, $NaHCO_3^o$ and $NaCO_3^-$. The input data required for this type of Diagram are : *Constants* - temperature, ionic strength, pK_{CaCO_3}, $pK_{Mg(OH)_2}$ and magnesium and sulphate concentrations; *Variables* - pH, calcium and Alkalinity. The units used for all the parameters except pH, are mmol ℓ^{-1} **. These Diagrams are applicable to effluents where ion pairing is significant, such as lime-treated wastewater.

The equilibrium dissociation constants (at 20°C) used in the calculations for constructing Diagrams including ion pairs, are

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*See Chapter 2, p. 16

**Table of conversions from mg ℓ^{-1} to mmol ℓ^{-1} and mg ℓ^{-1} (as $CaCO_3$) is given at the end of this Appendix.

$pK_{HCO_3^-} = 6,378$ .... (A1.1)

$pK_{CO_3^{2-}} = 10,37$ .... (A1.2)

$pK_{CaSO_4^o} = 2,289$ .... (A1.3)

$pK_{NaSO_4^-} = 1,003$ .... (A1.4)

$pK_{MgSO_4^o} = 2,301$ .... (A1.5)

$pK_{NaHCO_3^o} = 3,322$ .... (A1.6)

$pK_{NaCO_3^-} = 1,157$ .... (A1.7)

$pK_{MgHCO_3^+} = 0,768$ .... (A1.8)

$pK_{MgCO_3^o} = 3,399$ .... (A1.9)

$pK_{CaHCO_3^+} = 1,180$ .... (A1.10)

$pK_{CaCO_3^o} = 3,058$ .... (A1.11)

$pK_{MgOH^+} = 2,557$ .... (A1.12)

$pK_{CaOH^+} = 1,386$ .... (A1.13)

$pK_w = 14,17$ .... (A1.14)

and solubility products,

$pK_{CaCO_3(s)} = 8,35$ .... (A1.15)

$pK_{Mg(OH)_2(s)} = 10,32$ .... (A1.16)

A typical example illustrating the use of the Diagram for predicting the changes in a pure solution on lime addition is given below. A Diagram of the first type is used. However, application and use of the two types of Diagrams are identical.

1. Select a Diagram applicable to the specific problem under consideration, i.e. in terms of temperature, ionic strength and pK_{CaCO_3} value (see Figure A1.1).

2. Construct a table with columns for pH, Mg_T^{2+}, ΔMg_T^{2+} Alk.-Ca_T^{2+}, Alk., Ca_T^{2+}, Acid. and Lime, where

   Mg_T^{2+} - Residual total dissolved magnesium (mg ℓ^{-1} as $CaCO_3$)

   ΔMg_T^{2+} - Magnesium precipitated or removed from solution (mg ℓ^{-1} as $CaCO_3$)

   Alk. - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)

   Ca_T^{2+} - Residual total dissolved calcium (mg ℓ^{-1} as $CaCO_3$)

   Acid. - Total acidity (mg ℓ^{-1} as $CaCO_3$)

   Lime - Lime dosage (mg ℓ^{-1} as $CaCO_3$)

   A typical example of such a table is given in Table A1.1

3. Draw constant value lines on the Diagram for effluent pH, Alk. and Ca_T^{2+} values.

4. If these three lines intersect in one point the effluent is in equilibrium with calcium carbonate. If they do not intersect the effluent is either over or undersaturated with respect to calcite.

5.(a) If the water is *oversaturated*, the theoretical equilibrium state of this water may be calculated as follows :

(b) Determine the effluent Acidity by drawing a horizontal line (A) through the intersection of the constant pH and Alkalinity lines (point 1). The effluent acidity may be read from the intersection of this horizontal line with the acidity axis (Figure A1.1).

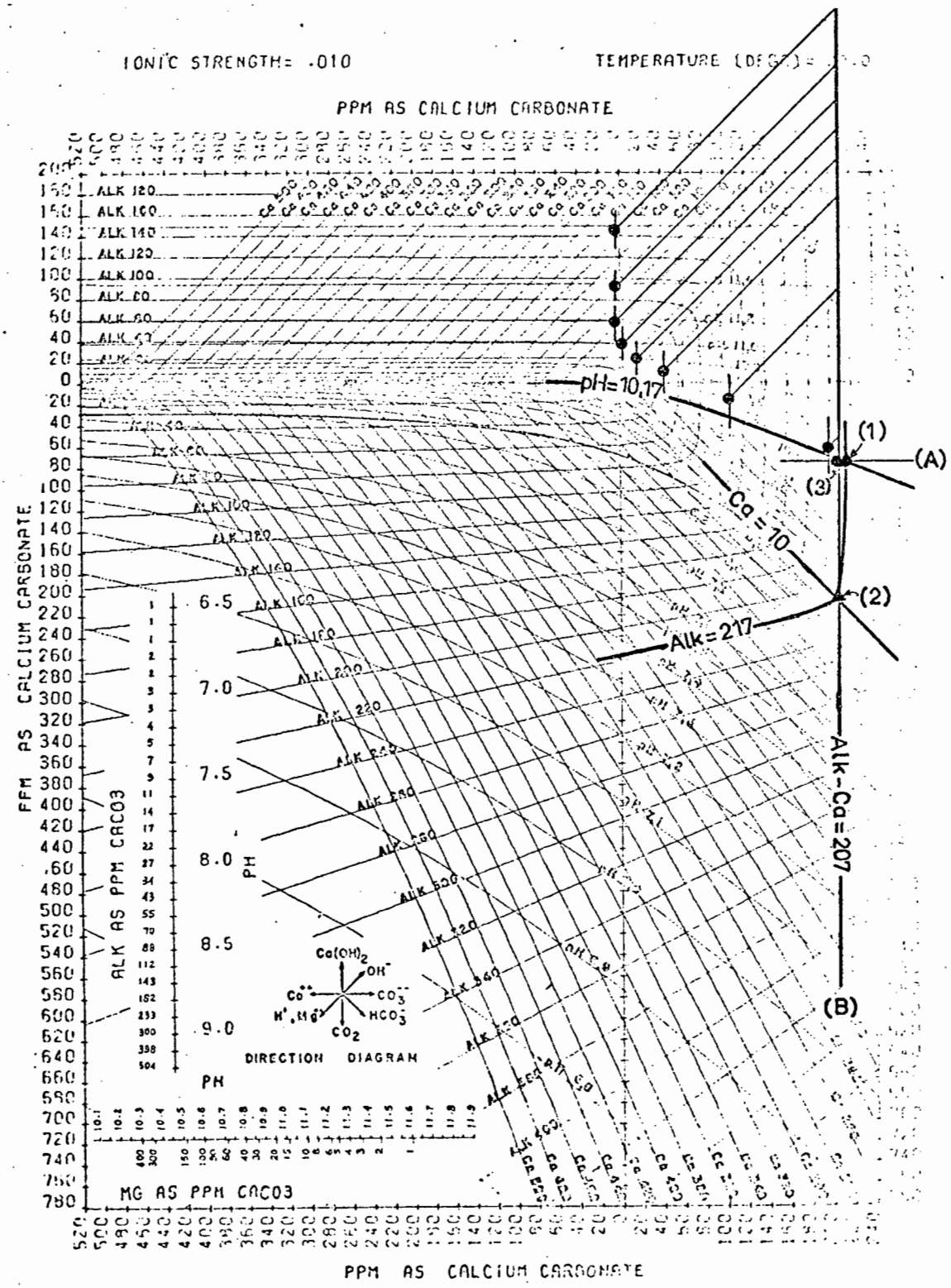


Figure A1.1. Plot on Modified Caldwell-Lawrence Diagram indicating changes in quality of secondary effluent affected by the addition of lime

Table A1.1

Predicted changes in effluent quality by using a Modified Caldwell-Lawrence Diagram

pH	Mg_T^{2+}	ΔMg_T^{2+}	(Alk.-Ca_T^{2+})	Alk.	Ca_T^{2+}	Acid.	Lime
10,17	218	0	207	217	10	75	0
10,15	218	0	207	208	1	75	0
10,20	210	8	199	200	1	46	29
10,40	115	103	104	106	2	-92	167
10,60	53	165	42	47	5	-178	253
10,80	25	193	14	33	19	-213	288
11,00	12	206	1	41	42	246	321
11,20	8	210	-3	60	63	272	347
11,40	8	210	-3	95	98	308	383
11,60	8	210	-3	150	153	362	437

All the parameters, excepting pH, are expressed in mg ℓ^{-1} as $CaCO_3$.

(c) Draw in a vertical line (B) through the point where the constant Alkalinity and Calcium lines intersect (Point 2).

(d) The equilibrium state is given by the intersection point of lines A and B, i.e. point 3.

6 (a) If the effluent is *undersaturated* with respect to calcite a theoretical equilibrium state can be achieved by the addition of lime. To find this state one must proceed by a method of trial and error :

(b) Decide on a small arbitrary addition of lime to the effluent, say 10 mg ℓ^{-1} lime (as $CaCO_3$). The Alkalinity and calcium values now increase by 10 and the Acidity value decreased by 10 mg ℓ^{-1} (as $CaCO_3$). The new pH is given by the intersection of the new Acidity and new Alkalinity lines. Check if the new pH, Alk. and Ca lines intersect. If they do, the theoretical equilibrium conditions have been defined, if not, continue with small theoretical lime additions until an equilibrium condition is achieved (intersection of pH, Alk and Ca lines).

7. Once the equilibrium condition has been established, the effect of any further additions of lime is given by moving upwards along the vertical line (B) through the point defining the equilibrium condition.

8. Should the effluent contain magnesium, a pH will be reached where any further lime addition will result in magnesium hydroxide precipitation.

9. The relationship between pH and residual total dissolved magnesium is given by a monograph on the MCLD.* Read off the residual magnesium value at pH intervals of 0,2 from this monograph. Tabulate in the table constructed in (2) above.

10. Calculate the masses of magnesium precipitated at these pH intervals and again tabulate.

11. Calculate the parameter $(Alk-Ca_T^{2+})$ for each pH by noting that for each mg ℓ^{-1} of Mg_T^{2+} precipitated this parameter decreases by 1 mg ℓ^{-1}, i.e. $(Alk-Ca_T^{2+})_{new} = (Alk-Ca_T^{2+})_{initial} - \Delta Mg_T^{2+}$.

12. Draw these $(Alk-Ca_T^{2+})$ lines in on the diagram and note where they intersect the pH line for which they were calculated.

---

*If an experimental relationship between pH and residual magnesium is known, this may also be used.

13. Read off the Alkalinity and Calcium values for these intersection points and tabulate.

14. The lime dosage to achieve the various equilibrium states may be found by drawing 45^{o} lines through the points for these states to intersect with the origional (Alk-Ca_T^{2+}) line where no magnesium precipitation had taken place. The Acidity value where these two lines intersect gives the total change in Acidity due to lime addition, i.e.

$$\text{Lime dose} = \text{Acid}_{new} - \text{Acid}_{initial}$$

By using the procedure described in (1) to (14), a specific effluent's response to lime treatment may be predicted in terms of the changes in pH, Alkalinity and residual total dissolved calcium which are affected by the various lime additions.

This page is followed by :

(1) A conversion table giving equivalents for mg ℓ^{-1}, mmol ℓ^{-1} and mg ℓ^{-1} (as $CaCO_3$).

(2) Two monographs for the relationships between pH and Mg_T^{2+} for $pK_{Mg(OH)_2}$ = 10,5 and 10,7.

(3) Five Modified Caldwell-Lawrence Diagrams for temperature = $20^{o}C$; μ = 0,015, SO_{4T}^{2-} = 0,64 mmol ℓ^{-1} and

(a) pK_{CaCO_3} = 8,35 and Mg_T^{2+} = 0,00 mmol ℓ^{-1}

(b) pK_{CaCO_3} = 8,35 and Mg_T^{2+} = 1,00 mmol ℓ^{-1}

(c) pK_{CaCO_3} = 7,10 and Mg_T^{2+} = 0,00 mmol ℓ^{-1}

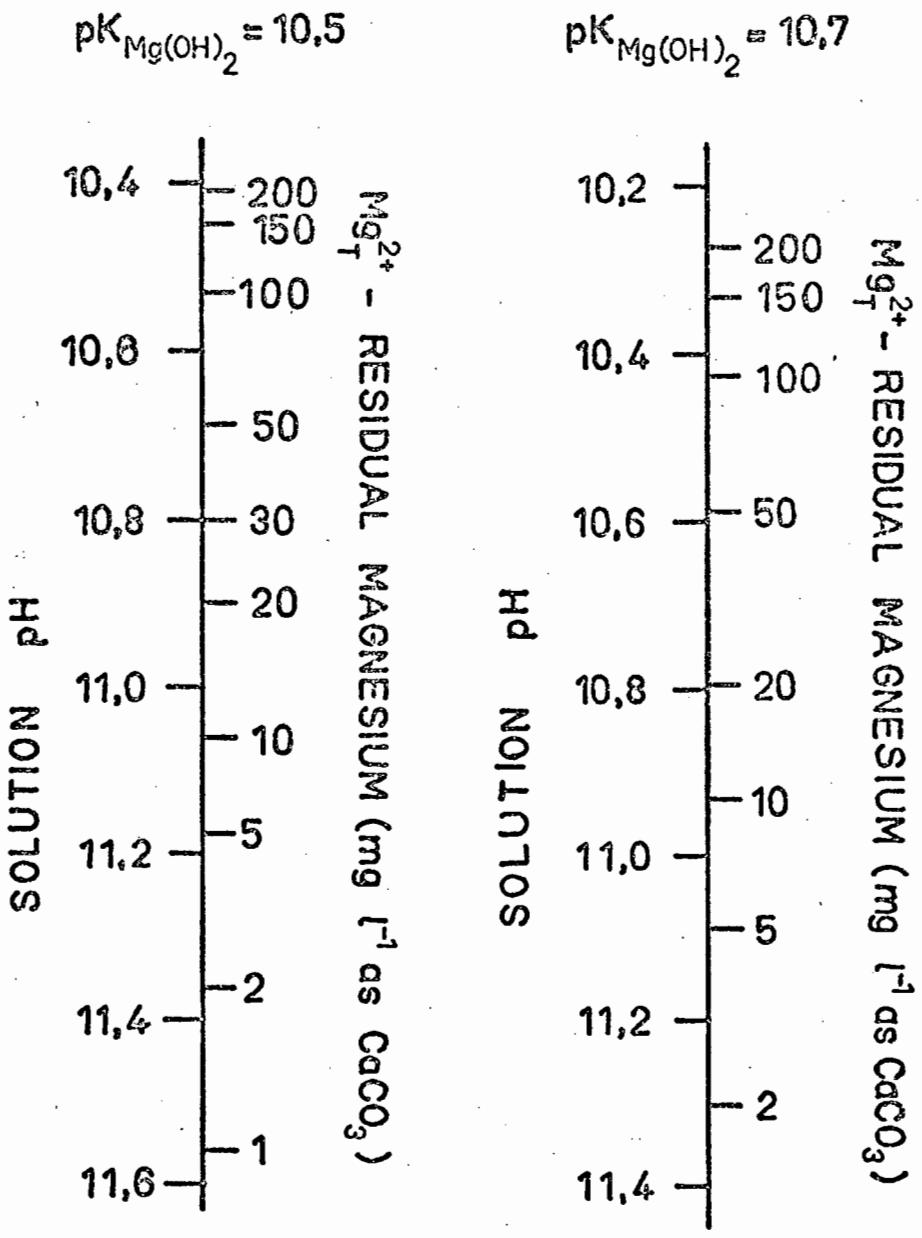
(d) pK_{CaCO_3} = 6,70 and Mg_T^{2+} = 0,00 mmol ℓ^{-1}

(e) pK_{CaCO_3} = 6,70 and Mg_T^{2+} = 1,00 mmol ℓ^{-1}

--- oOo ---

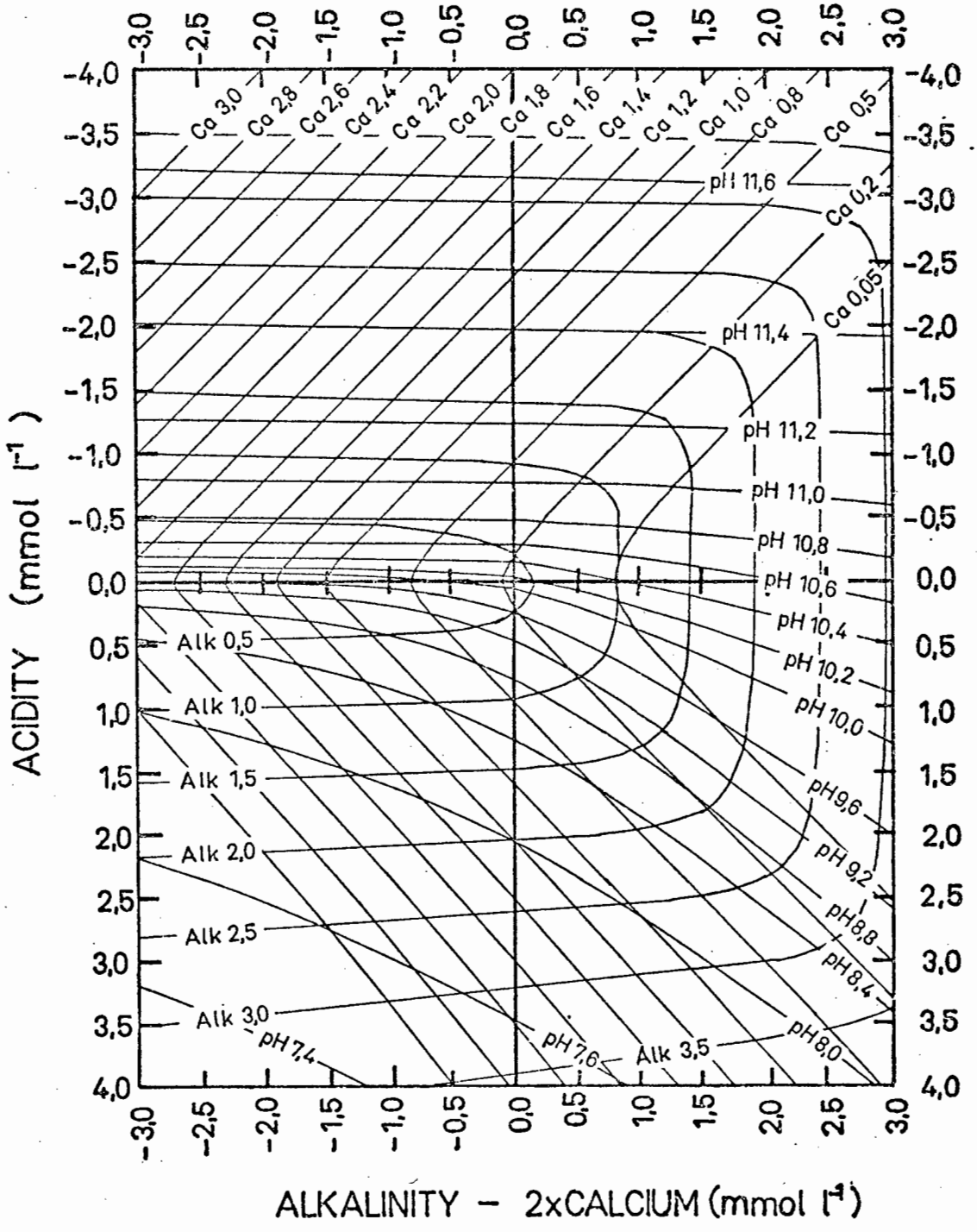
Table of conversions : mg ℓ^{-1} (as is) ≡ mmol ℓ^{-1} ≡ mg ℓ^{-1} (as $CaCO_3$)

Chemical (with concentration X mg ℓ^{-1})	Concentration of chemical as mmol ℓ^{-1}	Parameter	Concentration of parameter as mg ℓ^{-1} (as $CaCO_3$)
Acidity	X/50	Acid.	X
Alkalinity	X/50	Alk.	X
$CaCl_2$	X/116	Ca^{2+}_T	0,86.X
$CaCO_3$	X/100	Ca^{2+}_T	X
		CO^{2-}_{3T}	X
$Ca(OH)_2$	X/74	Ca^{2+}_T	1,35.X
		OH^-_T	1,35.X
CO_2	X/44	CO_2	2,27.X
H_2SO_4	X/98	H^+_T	1,02.X
$MgCl_2$	X/95	Mg^{2+}_T	1,05.X
Na_2CO_3	X/106	CO^{2-}_{3T}	0,94.X
$NaHCO_3$	X/84	HCO^-_{3T}	0,60.X
NaOH	X/40	OH^-_T	1,25.X



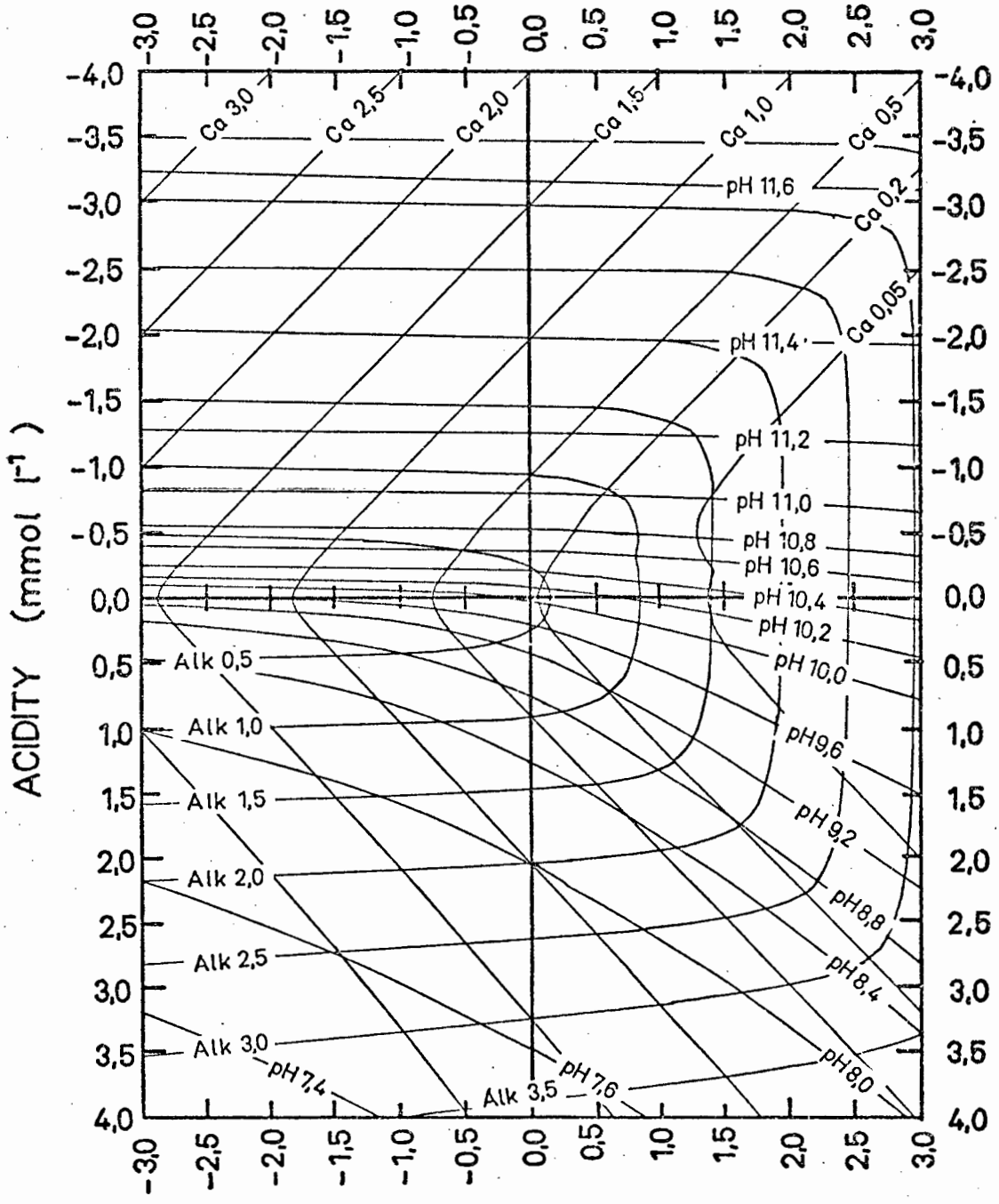
Monographs relating residual total dissolved magnesium concentration to effluent pH

pK_{CaCO_3} = 8,35 ; Mg^{2+}_T = 0,00*; SO^{2-}_{4T} = 0,64*;
TEMPERATURE = 20 °C ; μ = 0,015*



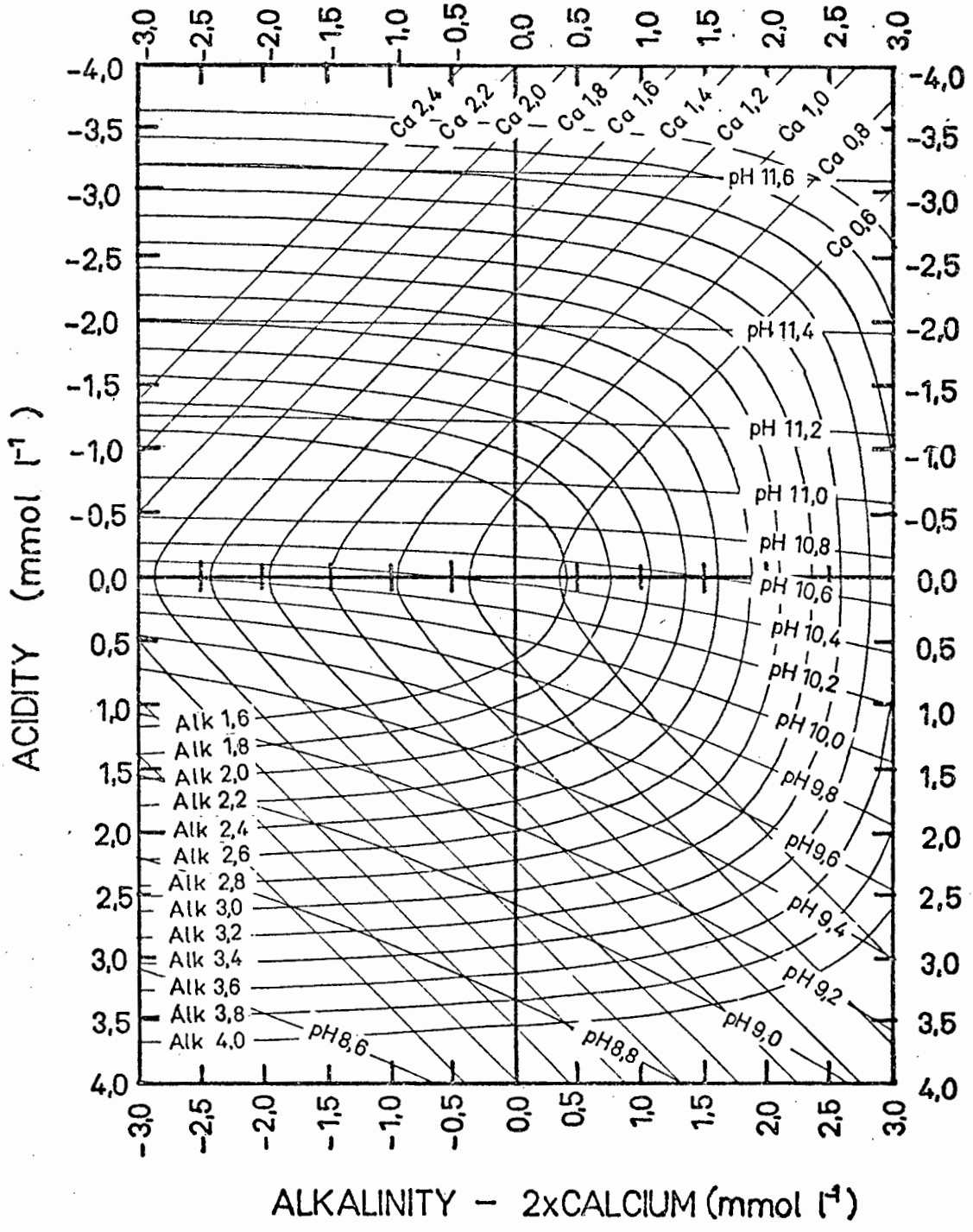
* mmol l^{-1}

pK_{CaCO_3} = 8,35 ; Mg^{2+}_T = 1,00*; SO^{2-}_{4T} = 0,64*;
TEMPERATURE = 20 °C ; μ = 0,015*.



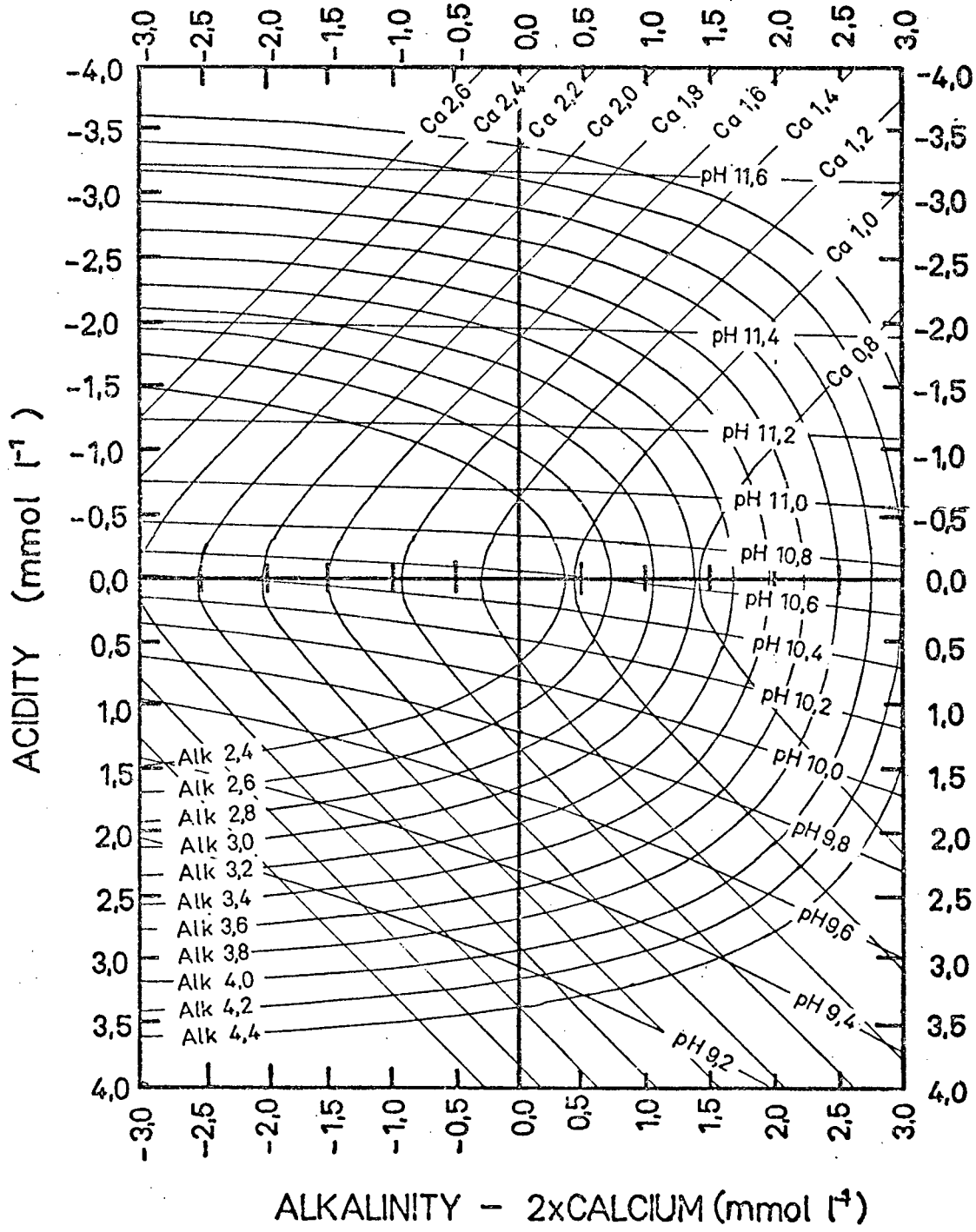
* mmol l^{-1}

$pK_{CaCO_3} = 7,10$; $Mg_T^{2+} = 0,00^*$; $SO_{4T}^{2-} = 0,64^*$;
TEMPERATURE = 20°C; $\mu = 0,015^*$

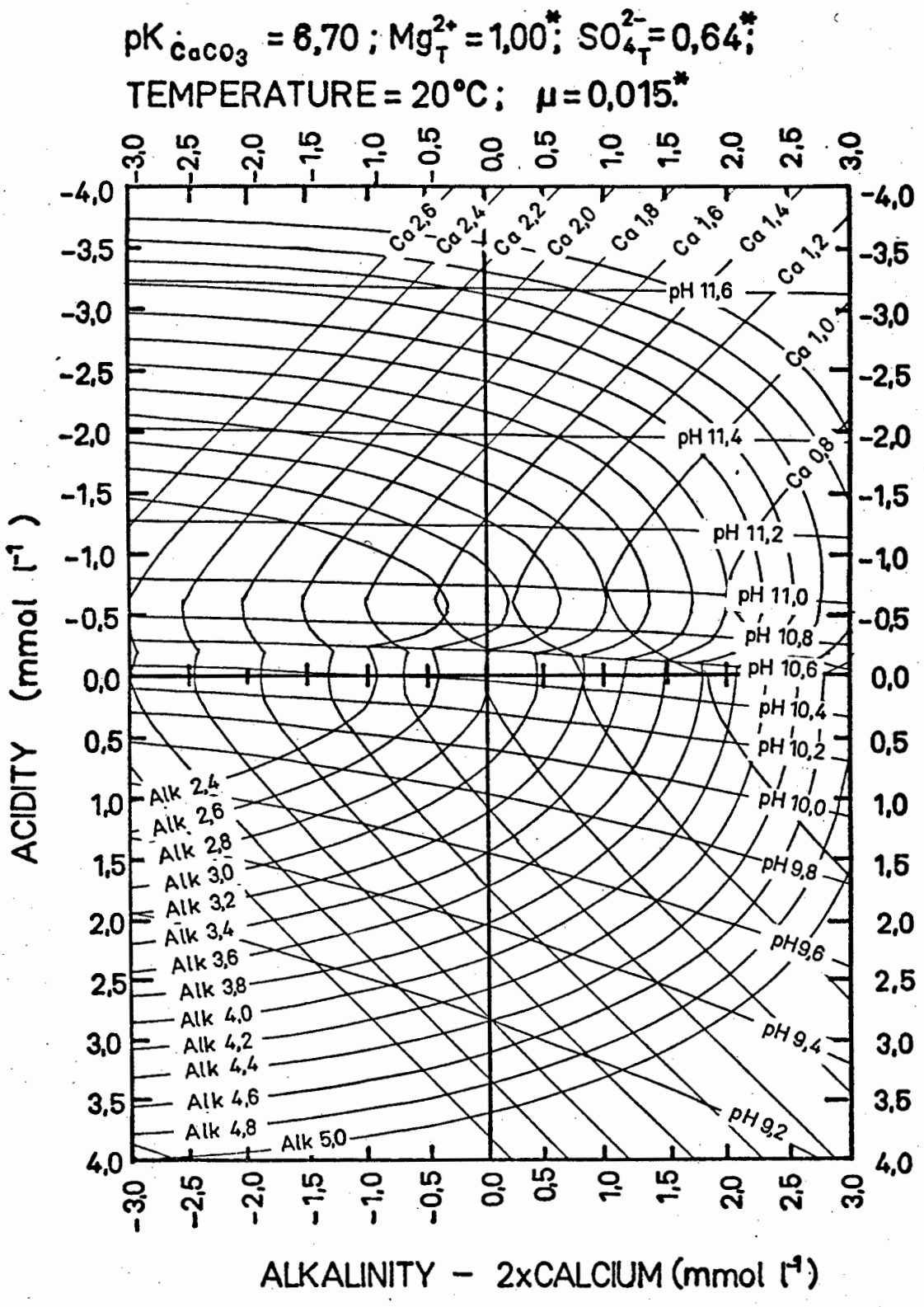


* mmol l^{-1}

$pK_{CaCO_3} = 6{,}70$; $Mg^{2+}_T = 0{,}00^*$; $SO^{2-}_{4T} = 0{,}64^*$;
TEMPERATURE = 20 °C ; $I = 0{,}015^*$



* mmol l^{-1}


pK CaCO3 = 6,70 ; Mg T 2+ = 1,00*; SO4 T 2- = 0,64*;
TEMPERATURE = 20°C ; μ = 0,015*
Ca 2,6
Ca 2,4
Ca 2,2
Ca 2,0
Ca 1,8
Ca 1,6
Ca 1,4
Ca 1,2
Ca 1,0
Ca 0,8
pH 11,6
pH 11,4
pH 11,2
pH 11,0
pH 10,8
pH 10,6
pH 10,4
pH 10,2
pH 10,0
pH 9,8
pH 9,6
pH 9,4
pH 9,2
Alk 2,4
Alk 2,6
Alk 2,8
Alk 3,0
Alk 3,2
Alk 3,4
Alk 3,6
Alk 3,8
Alk 4,0
Alk 4,2
Alk 4,4
Alk 4,6
Alk 4,8
Alk 5,0
ACIDITY (mmol l-1)
ALKALINITY − 2xCALCIUM (mmol l-1)
-3,0 -2,5 -2,0 -1,5 -1,0 -0,5 0,0 0,5 1,0 1,5 2,0 2,5 3,0
-4,0 -3,5 -3,0 -2,5 -2,0 -1,5 -1,0 -0,5 0,0 0,5 1,0 1,5 2,0 2,5 3,0 3,5 4,0

* mmol l^{-1}

APPENDIX 2

RAW DATA FOR EXPERIMENTS ON HOMOGENEOUS BATCH PRECIPITATION OF CALCIUM CARBONATE FROM SYNTHETIC SOLUTIONS*

Raw data collected during the investigation on homogeneous batch precipitation of calcium carbonate are listed below. The following codes are used,

NAHCO3 - Initial sodium bicarbonate concentration in the batch reactor (mol ℓ^{-1})

NAOH - Initial sodium hydroxide concentration in the batch reactor (mol ℓ^{-1})

CACL2 - Initial calcium chloride concentration in the batch reactor (mol ℓ^{-1})

Temperature - Reaction temperature as measured during the batch precipitation process (^{o}C)

TIME - Time interval elapsed (minutes) after the mixing of the basic reagent solutions, i.e. the CO_3^{2-} ($NaHCO_3$ + NaOH) and Ca^{2+} ($CaCl_2$) solutions.

PH - Reaction solution pH measured at a specific time interval.

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*See Chapter 3, p. 109

EXPERIMENT 7

NAHCO3 = 0,280 E-02; NAOH = 0,120 E-02; CACL2 = 0,200 E-02

TEMPERATURE = 20,5°C

TIME	PH	TIME	PH	TIME	PH	TIME	PH
0,0	9,980	4,0	9,560	8,0	9,125	14,0	8,815
0,5	9,735	4,5	9,500	8,5	9,080	15,0	8,795
1,0	9,745	5,0	9,440	9,0	9,045	29,0	8,670
1,5	9,740	5,5	9,380	9,5	9,005	39,0	8,645
2,0	9,725	6,0	9,320	10,0	8,980	50,0	8,615
2,5	9,700	6,5	9,265	11,0	8,925	60,0	8,595
3,0	9,660	7,0	9,220	12,0	8,880		
3,5	9,610	7,5	9,170	13,0	8,840		

EXPERIMENT 10

NAHCO3 = 0,280 E-02; NAOH = 0,115 E-02; CACL2 = 0,187 E-02

TEMPERATURE = 20,0°C

TIME	PH	TIME	PH	TIME	PH	TIME	PH
0,5	9,840	4,5	9,705	8,5	9,230	32,0	8,785
1,0	9,840	5,0	9,650	9,0	9,190	42,0	8,755
1,5	9,840	5,5	9,585	12,0	9,005		
2,0	9,840	6,0	9,515	14,0	8,945		
2,5	9,830	6,5	9,450	16,0	8,905		
3,0	9,815	7,0	9,385	18,0	8,875		
3,5	9,790	7,5	9,330	20,0	8,850		
4,0	9,750	8,0	9,280	22,0	8,835		

EXPERIMENT 13

NAHCO3 = 0,210 E-02; NAOH = 0,864 E-03; CACL2 = 0,141 E-02

TEMPERATURE = 19,2-20,9°C

TIME	PH	TIME	PH	TIME	PH	TIME	PH
0,0	10,030	4,0	9,795	8,0	9,575	14,0	9,220
0,5	9,810	4,5	9,780	8,5	9,540	15,0	9,180
1,0	9,820	5,0	9,760	9,0	9,505	17,0	9,110
1,5	9,820	5,5	9,735	9,5	9,470	22,0	9,020
2,0	9,820	6,0	9,710	10,0	9,435	29,5	8,940
2,5	9,820	6,5	9,680	11,0	9,375	59,5	9,820
3,0	9,810	7,0	9,645	12,0	9,315	89,5	8,765
3,5	9,805	7,5	9,610	13,0	9,265	149,5	8,710

EXPERIMENT 14

NAHCO3 = 0,160 E-02; NAOH = 0,672 E-03; CACL2 = 0,112 E-02

TEMPERATURE = 19,6 - 20,5 °C.

TIME	PH	TIME	PH	TIME	PH
0,0	10,030	7,0	9,760	18,0	9,295
1,0	9,840	8,0	9,720	20,0	9,245
2,0	9,840	9,0	9,675	25,0	9.155
3,0	9,840	10,0	9,625	35,0	9,080
4,0	9,830	12,0	9,520	95,0	8,990
5,0	9,815	14,0	9,430	155,0	8,905
6,0	9,790	16,0	9,355	215,0	8,855

EXPERIMENT 15

NAHCO3 = 0,140 E-02; NAOH = 0,576 E-03; CACL2 = 0,937 E-03

TEMPERATURE = 20,0-22,1°C

TIME	PH	TIME	PH	TIME	PH	TIME	PH
0,0	10,000	10,0	9,795	30,0	9,270	150,0	8,920
1,0	9,830	12,0	9,760	35,0	9,220	180,0	8,880
2,0	9,830	14,0	9,710	40,0	9,180	210,0	8,865
3,0	9,830	16,0	9,645	45,0	9,150	270,0	8,835
4,0	9,825	18,0	9,575	60,0	9,095	300,0	8,810
5,0	9,820	20,0	9,510	75,0	9,060	500,0	8,745
6,0	9,820	22,0	9,440	90,0	9,030	600,0	8,730
7,0	9,815	24,0	9,385	105,0	9,005	700,0	8,700
8,0	9,810	26,0	9,345	120,0	8,970	800,0	8,680
9,0	9,805	28,0	9,305	135,0	8,940	900,0	8,670

APPENDIX 3

DERIVATION OF EQUATIONS FOR $K_{CaCO_3^o}$ AND $K_{CaHCO_3^+}$ AND ASSOCIATED COMPUTER PROGRAMME FOR COMPUTING THESE CONSTANTS*

The values for the thermodynamic equilibrium constants $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$, are calculated from the following relationships,

$$K_{CaCO_3^o} = [Ca^{2+}][CO_3^{2-}].f_D^2/\{[Ca_T^{2+}] + [Ca^{2+}] + [H^+] + [Na^+] - ([OH^-] + 2[CO_3^{2+}] + [HCO_3^-] + [Cl^-])\} \quad .... \quad (A3.1)$$

and

$$K_{CaHCO_3^+} = [Ca^{2+}][HCO_3^-].f_D/\{[OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-] - (2[Ca^{2+}] + [H^+] + [Na^+])\} \quad .... \quad (A3.2)$$

The above relationships were arrived at as follows :

Equation for total dissolved calcium species,

$$[Ca_T^{2+}] = [CaCO_3^o] + [CaHCO_3^+] + [Ca^{2+}] \quad .... \quad (A3.3)$$

Equation for electro-neutrality,

$$2[Ca^{2+}] + [CaHCO_3^+] + [H^+] + [Na^+] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-]$$

---

*See Chapter 3, p. 111

i.e.

$$[CaHCO_3^+] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-] - (2[Ca^{2+}] + [H^+] + [Na^+]) \quad .... \quad (A3.4)$$

Substituting in (A3.3)

$$[Ca_T^{2+}] = [CaCO_3^o] + [Ca^{2+}] + [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-] - (2[Ca^{2+}] + [H^+] + [Na^+]) \quad .... \quad (A3.5)$$

i.e.

$$[CaCO_3^o] = [Ca_T^{2+}] + [Ca^{2+}] + [H^+] + [Na^+] - ([OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-])$$
$$= [Ca^{2+}][CO_3^{2-}].f_D^2/K_{CaCO_3^o} \quad .... \quad (A3.6)$$

i.e.

$$K_{CaCO_3^o} = [Ca^{2+}][CO_3^{2-}].f_D^2/\{[Ca_T^{2+}] + [Ca^{2+}] + [H^+] + [Na^+] - ([OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-])\} \quad .... \quad (A3.7)$$

Also $$K_{CaHCO_3^+} = \frac{[Ca^{2+}][CO_3^{2-}].f_D}{[CaHCO_3^+]} \quad .... \quad (A3.8)$$

Substitute into equation (A2.4)

$$K_{CaHCO_3^+} = [Ca^{2+}][HCO_3^-].f_D/\{[OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + [Cl^-] - (2[Ca^{+2}] + [H^+] + [Na^+])\} \quad .... \quad (A3.9)$$

PROGRAMME THERMK

Programme THERMK calculates the thermodynamic dissociation constants $K_{CaCO_3}^{o}$ and $K_{CaHCO_3}^{+}$ from reactant concentrations and the experimentally measured pH for ionic equilibrium during the induction period in experiments for homogeneous precipitation. The programme calculational procedure is as follows :

Thermodynamic Equilibrium Constants for the Carbonic System

The thermodynamic equilibrium constants K_1, K_2, K_w and K_{sp} are calculated as described in Appendix 9 (p. A9.1).

Calculation of Ionic Equilibrium Species Concentrations for Assumed Values of $K_{CaCO_3}^{o}$ and $K_{CaHCO_3}^{+}$

The species concentrations for a particular measured pH are calculated for ionic equilibrium, assuming the literature values of $K_{CaCO_3}^{o}$ and $K_{CaHCO_3}^{+}$. This is done as explained in Appendix 9 (p. A9.2).

Calculation of Self-Consistent Values for $K_{CaCO_3}^{o}$ and $K_{CaHCO_3}^{+}$

The assumed and calculated values of $K_{CaCO_3}^{o}$ are compared. They will very likely differ in magnitude. If they do differ, the value of $(K_{CaCO_3}^{o})_{ASS}$ is replaced by

$$(K_{CaCO_3}^{o})'_{ASS} = (K_{CaCO_3}^{o})_{ASS} \pm 0{,}005\ (K_{CaCO_3}^{o})_{ASS}$$

and the above calculation sequence is repeated. This whole process is repeated until the calculated and assumed values of $K_{CaCO_3}^{o}$ are within 1% of each other. This self consistant $K_{CaCO_3}^{o}$ value was taken as the experimental value for this constant.

An identical procedure was followed for the determination of the experimental $K_{CaHCO_3}^{+}$ value.

```
C*******************************************************************************
C      PROGRAM     THERMK
C*******************************************************************************
C      THIS PROGRAM CALCULATES THE THERMODYNAMIC DISSCCIATION
C      CONSTANTS :   KCACO3C     AND    KCAHCO3+.
C*******************************************************************************
C      DATA SET.
C
C      FIRST DATA CARD : IDENT   (I3).
C      IDENT IS THE EXPERIMENT IDENTIFICATION NUMBER.
C
C      SECOND DATA CARD :   NAHCC3,NAOH,CACL2.  (3E10.4).
C      NAHCO3 IS THE SODIUMBICARBONATE CONCENTRATION (MOLES/L) T=0.
C      NAOH IS THE SODIUM HYDROXIDE CONCENTRATICN (MOLES/L) T=0.
C      CACL2 IS THE CALCIUM CHLORIDE CONCENTRATICN (MOLES/L) T=0.
C
C      THIRD DATA CARD :   TS.   (E10.4).
C      TS IS THE TEMPERATURE IN DEGREES CELCIUS.
C
C      FORTH DATA CARD :   PH   (F10.4).
C      PH IS THE IONIC EQUILIBRIUM PH.
C*******************************************************************************
      REAL   NA,NAHCO3,NAOH,K1,K2,KW,KCO3O,KHCO3,KCACO3,KSP
      N=1
      M=3
      READ(N,234)  IDENT
234   FORMAT(I3)
      WRITE(M,235)   IDENT
235   FORMAT(1H1,'EXPERIMENT  NO.',I3,///)
      READ(N,1)    NAHCO3,NACH,CACL2
1     FORMAT(3E10.4)
      WRITE(M,2)   NAHCO3,NAOH,CACL2
2     FORMAT(1H ,'NAHCO3 = ',E10.4,4X,'NACH = ',E10.4,4X,
     1'CACL2 = ',E10.4,///)
      NA=NAHCO3+NAOH
      CT=NAHCO3
      CAT=CACL2
      CL=2.*CACL2
      READ(N,3)    TS
3     FORMAT(E10.4)
      WRITE(M,4)   TS
4     FORMAT(1H ,'TEMPERATURE = ',E10.4,'DEGREES CELCIUS',///)
C*******************************************************************************
C      CALCULATION OF EQUILIBRIUM CONSTANTS.
C*******************************************************************************
      TA=TS+273.
      PK1=(17052./TA)+215.21*ALOG(TA)/ALOG(10.)-(.12675*TA)-545.56
      K1=1./10.**PK1
```

```
      PK2=(2902.39/TA)+(.02379*TA)-6.498
      K2=1./10.**PK2
      PKW=(4787.3/TA)+(7.1321*ALOG(TA)/ALOG(10.))+(.01037*TA)-22.801
      KW=1./10.**PKW
      PKSPX=0.01183*TS+8.03
      KSP=1./10.**PKSPX
      KCO30=0.000631
      KHCO3=0.055
      WRITE(M,5)   K1,K2,KW,KHCO3,KSP,KCO30
5     FORMAT(1H ,'K1 = ',E10.4,4X,'K2 = ',E10.4,4X,'KW = ',E10.4,
     14X,'KCAHCO3+ = ',E10.4,4X,'KSP =',E10.4,4X,'KCACO30 = ',E10.4,
     2///)
      READ(N,200)   PH
200   FORMAT(F10.4)
      WRITE(M,201)   PH
201   FORMAT(1H ,'IONIC EQUILIBRIUM PH ',F10.4,///)
C*****************************************************************
C     CALCULATION OF SPECIES CONCENTRATIONS FOR ASSUMED
C     KCACO30 AND KCAHCO3+ VALUES.
C*****************************************************************
      NUMB1=1
      NUMB2=2
212   QQQQ=0.
506   RUN10=1.
      RUN11=1.
      H2CO3=0.
      FMXX=0.912
      FDXX=0.692
      AH=-PH-ALOG10(FMXX)
      AH=-AH
      H=1./10.**AH
      HCO3=0.0017
307   CA=CAT/(1.+(HCO3*FDXX/KHCO3)+(K2*FDXX*HCO3/(KCO30*H)))
      CO3=CA+CT-HCO3-H2CO3-CAT
      IF(CO3-0.0)    350,350,351
350   ZZZZ=HCO3
      HCO3=ZZZZ-0.0001
      GO TO 307
351   CONTINUE
      H2CO3=H*HCO3*(FMXX**2.)/K1
      CAHCO3=CA*HCO3*FDXX/KHCO3
      CACO30=CA*CO3*(FDXX**2.)/KCO30
      OH=KW/(H*(FMXX**2.))
      CHCO3=NA+2.*CA+H+CAHCO3-CL-OH-2.*CO3
      U=0.5*(NA+H+4.*CA+CAHCO3+CL+OH+HCO3+4.*CO3)
      F=((SQRT(U)/(1.+SQRT(U)))-0.3*U)
      AFMXX=0.5*F
      FMXX=1./10.**AFMXX
```

```
      AFDXX=2.*F
      FDXX=1./10.**AFDXX
      RUN101=2.
      IF(RUN10-RUN101)     300,300,305
300   IF(HCO3-CHCO3)     303,304,305
303   Q1=0.01*HCO3
      ZHCO3=HCO3
      HCO3=ZHCO3-Q1
      GO TO 307
305   RUN10=3.
      RUN111=2.
      IF(RUN11-RUN111)    308,308,309
308   Q2=HCO3-CHCO3
      RUN11=3.
309   IF(HCO3-CHCO3)     403,311,405
405   HCO3PO=HCO3
403   Q6=0.1*Q2
      Q7=HCO3+Q6
      Q8=0.0001*HCO3
      IF(Q6-Q8)     311,311,325
325   IF(HCO3-CHCO3)    406,311,408
408   HCO3=Q7
      GO TO 307
406   HCO3=HCO3PO+0.01*Q2
      ZQ2=Q2
      Q2=0.01*ZQ2
      GO TO 307
304   CONTINUE
311   CONTINUE
C*************************************************************************
C     CALCULATION OF THERMODYNAMIC CONSTANTS.
C*************************************************************************
203   ZK1=CA*CO3*(FDXX**2)
      ZK2=CAT+CA+H+NA-OH-2.*CO3-HCO3-CL
      CKCO30=ZK1/ZK2
      ZK3=CA*HCO3*FDXX
      ZK4=OH+2.*CO3+HCO3+CL-2.*CA-H-NA
      CKHCO3=ZK3/ZK4
      ZK5=KCO30-CKCO30
      ZABS=ABS(ZK5)
      ZK6=0.01*KCO30
      IF(ZABS-ZK6)    206,207,208
208   IF(KCO30-CKCO30)     209,210,211
209   ZK7=KCO30
      KCO30=ZK7-0.005*ZK7
      GO TO 212
211   ZK8=KCO30
      KCO30=ZK8+0.005*ZK8
```

```
      GO TO 212
210   CONTINUE
206   CONTINUE
207   CONTINUE
215   CONTINUE
214   CONTINUE
204   CONTINUE
202   CONTINUE
      WRITE(M,205)   CKCO3O,CKHCO3
205   FORMAT(1H ,'CALCULATED KCACO3O = ',E10.4,2X,'CALCULATED  KCAHCO3
     1 ',E10.4///)
      CALL EXIT
      END
```

APPENDIX 4

RAW DATA FOR EXPERIMENTS ON HETEROGENEOUS BATCH PRECIPITATION OF CALCIUM CARBONATE FROM SYNTHETIC SOLUTIONS*

Raw data collected during the investigation on heterogeneous batch precipitaiton of calcium carbonate are listed below. The major variable under study in each set of experiments is also indicated,

Experiments 1C-7C - Effect of $CaCO_3$ seed mass (Hopkin and Williams $CaCO_3$)

Experiments 12C-26C - Effect of different reactant concentrations (Hopkin and Williams $CaCO_3$)

Experiments 1 - 20 - Effect of temperature (Merck $CaCO_3$)

Experiments 22 - 29 - Effect of different reactant concentrations (Merck $CaCO_3$)

Experiments 30 - 35 - Effect of mixing intensity (Merck $CaCO_3$)

Experiments 40 - 56 - Effect of different reactant concentrations (Merck $CaCO_3$)

Experiments 34H - 43H - Effect of $CaCO_3$ seed mass (Merck, $CaCO_3$)

The following codes are used,

NAHCO3 - Initial total sodium bicarbonate concentration (mol ℓ^{-1})

NAOH - Initial total sodium hydroxide concentration (mol ℓ^{-1})

CACL2 - Initial total calcium chloride concentration (mol ℓ^{-1})

TEMPERATURE - Average batch reaction temperature (^{o}C)

TIME - Time interval after mixing reagents (min)

PH - Reaction solution pH

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*See Chapter 3, p. 130

EXPERIMENT NO.1C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 24.7 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 50.

TIME	PH	TIME	PH
0.1000	9.7840	3.4000	9.5120
0.2000	9.7760	3.6000	9.4880
0.3000	9.7680	3.8000	9.4720
0.4000	9.7600	4.0000	9.4480
0.5000	9.7560	4.2000	9.4320
0.6000	9.7520	4.4000	9.4080
0.7000	9.7440	4.6000	9.3880
0.8000	9.7400	4.8000	9.3660
0.9000	9.7320	5.0000	9.3440
1.0000	9.7240	5.2000	9.3280
1.1000	9.7160	5.4000	9.3040
1.2000	9.7120	5.6000	9.2880
1.3000	9.7040	5.8000	9.2640
1.4000	9.6960	6.0000	9.2480
1.5000	9.6880	6.5000	9.2000
1.6000	9.6800	7.0000	9.1520
1.7000	9.6720	7.5000	9.1120
1.8000	9.6640	8.0000	9.0640
1.9000	9.6520	8.5000	9.0200
2.0000	9.6400	9.0000	8.9840
2.1000	9.6320	9.5000	8.9520
2.2000	9.6240	10.0000	8.9200
2.3000	9.6160	10.5000	8.8840
2.4000	9.6040	11.0000	8.8560
2.5000	9.5960	11.5000	8.8240
2.6000	9.5840	12.0000	8.8000
2.7000	9.5760	12.5000	8.7760
2.8000	9.5680		
2.9000	9.5560		
3.0000	9.5440		
3.2000	9.5280		

EXPERIMENT NO.2C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 25.0 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 100.

TIME	PH	TIME	PH
0.1000	9.7730	2.9000	9.3810
0.2000	9.7610	3.0000	9.3650
0.3000	9.7530	3.2000	9.3370
0.4000	9.7370	3.4000	9.3130
0.5000	9.7250	3.6000	9.2850
0.6000	9.7130	3.8000	9.2570
0.7000	9.6970	4.0000	9.2370
0.8000	9.6850	4.2000	9.2090
0.9000	9.6730	4.4000	9.1850
1.0000	9.6570	4.6000	9.1570
1.1000	9.6450	4.8000	9.1330
1.2000	9.6330	5.0000	9.1050
1.3000	9.6170	5.2000	9.0850
1.4000	9.6010	5.4000	9.0650
1.5000	9.5850	5.6000	9.0410
1.6000	9.5690	5.8000	9.0170
1.7000	9.5530	6.0000	8.9930
1.8000	9.5410	6.2000	8.9730
1.9000	9.5250	6.4000	8.9530
2.0000	9.5130	6.6000	8.9330
2.1000	9.4970	6.8000	8.9130
2.2000	9.4810	7.0000	8.8930
2.3000	9.4690	7.2000	8.8770
2.4000	9.4530	7.4000	8.8570
2.5000	9.4410	7.6000	8.8410
2.6000	9.4250		
2.7000	9.4090		
2.8000	9.3930		

EXPERIMENT NO.3C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 25.6 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 150.

TIME	PH	TIME	PH
0.1000	9.7640	3.2000	9.2200
0.2000	9.7440	3.4000	9.1880
0.3000	9.7240	3.6000	9.1560
0.4000	9.7120	3.8000	9.1280
0.5000	9.6880	4.0000	9.1040
0.6000	9.6680	4.2000	9.0760
0.7000	9.6520	4.4000	9.0440
0.8000	9.6280	4.6000	9.0200
0.9000	9.6120	4.8000	8.9920
1.0000	9.5960	5.0000	8.9640
1.1000	9.5760	5.2000	8.9400
1.2000	9.5600	5.4000	8.9120
1.3000	9.5440	5.6000	8.8880
1.4000	9.5280	5.8000	8.8680
1.5000	9.5080	6.0000	8.8440
1.6000	9.4880	6.2000	8.8200
1.7000	9.4720	6.4000	8.8000
1.8000	9.4520	6.6000	8.7760
1.9000	9.4360	6.8000	8.7560
2.0000	9.4160	7.0000	8.7400
2.1000	9.4000	7.2000	8.7200
2.2000	9.3800	7.4000	8.7000
2.3000	9.3640	7.6000	8.6840
2.4000	9.3480		
2.5000	9.3320		
2.6000	9.3160		
2.7000	9.3000		
2.8000	9.2840		
2.9000	9.2680		
3.0000	9.2520		

EXPERIMENT NO.4C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 25.0 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 200.

TIME	PH	TIME	PH
0.1000	9.7650	2.4000	9.2810
0.2000	9.7490	2.5000	9.2610
0.3000	9.7290	2.6000	9.2450
0.4000	9.7050	2.7000	9.2250
0.5000	9.6850	2.8000	9.2050
0.6000	9.6610	2.9000	9.1850
0.7000	9.6410	3.0000	9.1690
0.8000	9.6210	3.2000	9.1290
0.9000	9.5970	3.4000	9.0970
1.0000	9.5730	3.6000	9.0650
1.1000	9.5530	3.8000	9.0330
1.2000	9.5330	4.0000	9.0010
1.3000	9.5090	4.2000	8.9690
1.4000	9.4850	4.4000	8.9370
1.5000	9.4650	4.6000	8.9090
1.6000	9.4410	4.8000	8.8810
1.7000	9.4210	5.0000	8.8570
1.8000	9.4010	5.2000	8.8290
1.9000	9.3810	5.4000	8.8050
2.0000	9.3610	5.6000	8.7770
2.1000	9.3410	5.8000	8.7530
2.2000	9.3210		
2.3000	9.3010		

EXPERIMENT NO.5C

NAHCO3 = 0.1983E-02 NAOH = 0.948CE-03 CACL2 = 0.2046E-02

TEMPERATURE = 25.0 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 250.0000

TIME	PH	TIME	PH
0.1000	9.7690	2.6000	9.2010
0.2000	9.7450	2.7000	9.1770
0.3000	9.7250	2.8000	9.1610
0.4000	9.7010	2.9000	9.1410
0.5000	9.6770	3.0000	9.1610
0.6000	9.6530	3.2000	9.0890
0.7000	9.6250	3.4000	9.0490
0.8000	9.6050	3.6000	9.0170
0.9000	9.5810	3.8000	8.9770
1.0000	9.5570	4.0000	8.9490
1.1000	9.5290	4.2000	8.9130
1.2000	9.5050	4.4000	8.8890
1.3000	9.4850	4.6000	8.8570
1.4000	9.4610	4.8000	8.8250
1.5000	9.4410	5.0000	8.7970
1.6000	9.4170	5.2000	8.7650
1.7000	9.3890	5.4000	8.7410
1.8000	9.3690	5.6000	8.7170
1.9000	9.3450	5.8000	8.6930
2.0000	9.3250	6.0000	8.6730
2.1000	9.3010	6.2000	8.6490
2.2000	9.2810	6.4000	8.6250
2.3000	9.2610	6.6000	8.6090
2.4000	9.2370	6.8000	8.5850
2.5000	9.2210		

EXPERIMENT NO.6C

NAHCO3 = 0.1983E-02 NAOH = C.948CE-03 CACL2 = 0.2046E-02

TEMPERATURE = 25.0 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 300.0000

TIME	PH	TIME	PH
0.1000	9.7610	2.4000	9.1930
0.2000	9.7290	2.5000	9.1690
0.3000	9.7010	2.6000	9.1530
0.4000	9.6770	2.7000	9.1290
0.5000	9.6450	2.8000	9.1130
0.6000	9.6170	2.9000	9.0930
0.7000	9.5930	3.0000	9.0770
0.8000	9.5690	3.2000	9.0370
0.9000	9.5410	3.4000	9.0010
1.0000	9.5170	3.6000	8.9690
1.1000	9.4890	3.8000	8.9370
1.2000	9.4650	4.0000	8.9050
1.3000	9.4410	4.2000	8.8730
1.4000	9.4170	4.4000	8.8370
1.5000	9.3930	4.6000	8.8050
1.6000	9.3690	4.8000	8.7730
1.7000	9.3450	5.0000	8.7450
1.8000	9.3210	5.2000	8.7130
1.9000	9.3010	5.4000	8.6890
2.0000	9.2810	5.6000	8.6570
2.1000	9.2570	5.8000	8.6330
2.2000	9.2370		
2.3000	9.2170		

EXPERIMENT NO.7C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 24.8 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 350.0000

TIME	PH	TIME	PH
0.1000	9.7590	2.1000	9.1430
0.2000	9.7270	2.2000	9.1190
0.3000	9.6990	2.3000	9.0950
0.4000	9.6670	2.4000	9.0670
0.5000	9.6390	2.5000	9.0430
0.6000	9.6030	2.6000	9.0190
0.7000	9.5670	2.7000	8.9950
0.8000	9.5350	2.8000	8.9710
0.9000	9.5030	2.9000	8.9510
1.0000	9.4670	3.0000	8.9270
1.1000	9.4350	3.2000	8.8830
1.2000	9.4030	3.4000	8.8390
1.3000	9.3710	3.6000	8.7990
1.4000	9.3430	3.8000	8.7590
1.5000	9.3150	4.0000	8.7230
1.6000	9.2830	4.2000	8.6870
1.7000	9.2510	4.4000	8.6550
1.8000	9.2270	4.6000	8.6230
1.9000	9.1990	4.8000	8.5910
2.0000	9.1710		

EXPERIMENT NO.12C

NAHCO3 = 0.1958E-02 NAOH = 0.1909E-03 CACL2 = 0.2050E-02

TEMPERATURE = 25.4 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.2000	8.8220	2.1000	8.2100
0.3000	8.7820	2.2000	8.1900
0.4000	8.7420	2.3000	8.1700
0.5000	8.7020	2.4000	8.1500
0.6000	8.6660	2.5000	8.1340
0.7000	8.6300	2.6000	8.1180
0.8000	8.5940	2.7000	8.1020
0.9000	8.5580	2.8000	8.0860
1.0000	8.5220	2.9000	8.0700
1.1000	8.4860	3.0000	8.0620
1.2000	8.4540	3.2000	8.0340
1.3000	8.4260	3.4000	8.0100
1.4000	8.3940	3.6000	7.9900
1.5000	8.3660	3.8000	7.9740
1.6000	8.3380	4.0000	7.9500
1.7000	8.3100	4.2000	7.9340
1.8000	8.2860	4.4000	7.9220
1.9000	8.2580	4.6000	7.9060
2.0000	8.2340	4.8000	7.8940

EXPERIMENT NO.13C

NAHCO3 = 0.1958E-02 NAOH = 0.3E18E-03 CACL2 = 0.2050E-02

TEMPERATURE = 25.4 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.1000	9.1580	1.8000	8.4780
0.2000	9.1140	1.9000	8.4460
0.3000	9.0700	2.0000	8.4180
0.4000	9.0260	2.1000	8.3860
0.5000	8.9820	2.2000	8.3580
0.6000	8.9380	2.3000	8.3340
0.7000	8.8900	2.4000	8.3100
0.8000	8.8460	2.5000	8.2860
0.9000	8.8060	2.6000	8.2660
1.0000	8.7620	2.7000	8.2460
1.1000	8.7220	2.8000	8.2220
1.2000	8.6820	2.9000	8.2020
1.3000	8.6460	3.0000	8.1860
1.4000	8.6100	3.2000	8.1500
1.5000	8.5740	3.4000	8.1180
1.6000	8.5420	3.6000	8.0900
1.7000	8.5100	3.8000	8.0660

EXPERIMENT NO.14C

NAHCO3 = 0.1958E-02 NAOH = 0.5727E-03 CACL2 = 0.2050E-02

TEMPERATURE = 25.3 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.1000	9.4000	2.0000	8.6360
0.2000	9.3560	2.1000	8.6040
0.3000	9.3120	2.2000	8.5760
0.4000	9.2720	2.3000	8.5440
0.5000	9.2240	2.4000	8.5120
0.6000	9.1760	2.5000	8.4940
0.7000	9.1360	2.6000	8.4560
0.8000	9.0880	2.7000	8.4320
0.9000	9.0480	2.8000	8.4080
1.0000	9.0000	2.9000	8.3840
1.1000	8.9640	3.0000	8.3600
1.2000	8.9200	3.2000	8.3200
1.3000	8.8800	3.4000	8.2800
1.4000	8.8440	3.6000	8.2400
1.5000	8.8060	3.8000	8.2080
1.6000	8.7680	4.0000	8.1800
1.7000	8.7360	4.2000	8.1520
1.8000	8.7000	4.4000	8.1280
1.9000	8.6720		

EXPERIMENT NO.15C

NAHCO3 = 0.1958E-02 NAOH = 0.7636E-03 CACL2 = 0.2050E-02

TEMPERATURE = 25.1 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.1330	9.6050	1.4670	9.0610
0.2000	9.5770	1.5330	9.0370
0.2670	9.5490	1.6000	9.0130
0.3330	9.5210	1.6670	8.9890
0.4000	9.4890	1.7330	8.9650
0.4670	9.4610	1.8000	8.9410
0.5330	9.4370	1.8670	8.9210
0.6000	9.4050	1.9330	8.9010
0.6670	9.3730	2.0000	8.8770
0.7330	9.3450	2.2000	8.8770
0.8000	9.3170	2.4000	8.7570
0.8670	9.2930	2.6000	8.7010
0.9330	9.2610	2.8000	8.6450
1.0000	9.2370	3.0000	8.5890
1.0670	9.2130	3.2000	8.5450
1.1330	9.1890	3.4000	8.5010
1.2000	9.1650	3.6000	8.4610
1.2670	9.1410	3.8000	8.4250
1.3330	9.1170		
1.4000	9.0930		

EXPERIMENT NO.16C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 25.0 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.0667	9.7490	1.4667	9.1690
0.1333	9.7170	1.5333	9.1410
0.2000	9.6850	1.6000	9.1170
0.2667	9.6530	1.6667	9.0970
0.3333	9.6250	1.7333	9.0730
0.4000	9.5930	1.8000	9.0490
0.4667	9.5650	1.8667	9.0330
0.5333	9.5330	1.9333	9.0010
0.6000	9.5050	2.0000	8.9850
0.6667	9.4730	2.2000	8.9210
0.7333	9.4490	2.4000	8.8650
0.8000	9.4210	2.6000	8.8090
0.8667	9.3930	2.8000	8.7530
0.9333	9.3650	3.0000	8.7050
1.0000	9.3410	3.2000	8.6570
1.0667	9.3170	3.4000	8.6090
1.1333	9.2930	3.6000	8.5730
1.2000	9.2690	3.8000	8.5330
1.2667	9.2450		
1.3333	9.2210		
1.4000	9.1930		

EXPERIMENT NO.17C

NAHCO3 = 0.1958E-02 NAOH = 0.1145E-02 CACL2 = 0.2050E-02

TEMPERATURE = 25.2 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.0670	9.9270	1.3330	9.3870
0.1330	9.9030	1.4000	9.3590
0.2000	9.8750	1.4670	9.3350
0.2670	9.8470	1.5330	9.3110
0.3330	9.8190	1.6000	9.2870
0.4000	9.7870	1.6670	9.2630
0.4670	9.7550	1.7330	9.2390
0.5330	9.7230	1.8000	9.2150
0.6000	9.6950	1.8670	9.1990
0.6670	9.6630	1.9330	9.1750
0.7330	9.6310	2.0000	9.1510
0.8000	9.6030	2.2000	9.0870
0.8670	9.5750	2.4000	9.0310
0.9330	9.5430	2.6000	8.9750
1.0000	9.5190	2.8000	8.9270
1.0670	9.4910	3.0000	8.8830
1.1330	9.4670	3.2000	8.8390
1.2000	9.4390	3.4000	8.7990
1.2670	9.4110	3.6000	8.7630

EXPERIMENT NO.18C

NAHCO3 = 0.1958E-02 NAOH = 0.1336E-02 CACL2 = 0.2050E-02

TEMPERATURE = 25.1 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.0670	10.0790	1.4000	9.6070
0.1330	10.0630	1.4670	9.5830
0.2000	10.0390	1.5330	9.5630
0.2670	10.0190	1.6000	9.5430
0.3330	9.9950	1.6670	9.5230
0.4000	9.9670	1.7330	9.5030
0.4670	9.9510	1.8000	9.4830
0.5330	9.9150	1.8670	9.4630
0.6000	9.8910	1.9330	9.4470
0.6670	9.8670	2.0000	9.4230
0.7330	9.8430	2.2000	9.3710
0.8000	9.8190	2.4000	9.3270
0.8670	9.7950	2.6000	9.2750
0.9330	9.7670	2.8000	9.2270
1.0000	9.7470	3.0000	9.1830
1.0670	9.7190	3.2000	9.1390
1.1330	9.6950	3.4000	9.0990
1.2000	9.6710	3.6000	9.0630
1.2670	9.6470	3.8000	9.0270
1.3330	9.6270		

EXPERIMENT NO.19C

NAHCO3 = 0.1958E-02 NAOH = 0.1527E-02 CACL2 = 0.2050E-02

TEMPERATURE = 25.2 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.1000	10.2120	2.1000	9.6360
0.2000	10.1840	2.2000	9.6160
0.3000	10.1520	2.3000	9.5960
0.4000	10.1200	2.4000	9.5720
0.5000	10.0880	2.5000	9.5520
0.6000	10.0520	2.6000	9.5320
0.7000	10.0200	2.7000	9.5120
0.8000	9.9920	2.8000	9.4960
0.9000	9.9600	2.9000	9.4760
1.0000	9.9280	3.0000	9.4600
1.1000	9.8960	3.2000	9.4240
1.2000	9.8680	3.4000	9.3920
1.3000	9.8400	3.6000	9.3640
1.4000	9.8120	3.8000	9.3320
1.5000	9.7840	4.0000	9.3080
1.6000	9.7560	4.2000	9.2800
1.7000	9.7320	4.4000	9.2560
1.8000	9.7120	4.6000	9.2360
1.9000	9.6840	4.8000	9.2160
2.0000	9.6600		

EXPERIMENT NO.20C

NAHCO3 = 0.1958E-02 NAOH = 0.1718E-02 CACL2 = 0.2050E-02

TEMPERATURE = 25.2 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.1000	10.3560	2.0000	9.9400
0.2000	10.3360	2.1000	9.9240
0.3000	10.3120	2.2000	9.9080
0.4000	10.2880	2.3000	9.8920
0.5000	10.2640	2.4000	9.8760
0.6000	10.2360	2.5000	9.8640
0.7000	10.2120	2.6000	9.8520
0.8000	10.1880	2.7000	9.8360
0.9000	10.1640	2.8000	9.8240
1.0000	10.1400	2.9000	9.8080
1.1000	10.1160	3.0000	9.7960
1.2000	10.0920	3.2000	9.7720
1.3000	10.0680	3.4000	9.7480
1.4000	10.0480	3.6000	9.7248
1.5000	10.0280	3.8000	9.7080
1.6000	10.0080	4.0000	9.6880
1.7000	9.9920	4.2000	9.6680
1.8000	9.9720	4.4000	9.6520
1.9000	9.9560	4.6000	9.6360
		4.8000	9.6200

EXPERIMENT NO.21C

NAHCO3 = 0.1958E-02 NAOH = 0.1909E-02 CACL2 = 0.2050E-02

TEMPERATURE = 25.3 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0000

TIME	PH	TIME	PH
0.1000	10.4800	2.1000	10.1720
0.2000	10.4640	2.2000	10.1600
0.3000	10.4440	2.3000	10.1520
0.4000	10.4240	2.4000	10.1400
0.5000	10.4080	2.5000	10.1360
0.6000	10.3880	2.6000	10.1280
0.7000	10.3720	2.7000	10.1160
0.8000	10.3520	2.8000	10.1080
0.9000	10.3360	2.9000	10.1000
1.0000	10.3160	3.0000	10.0960
1.1000	10.3000	3.2000	10.0800
1.2000	10.2880	3.4000	10.0680
1.3000	10.2720	3.6000	10.0520
1.4000	10.2600	3.8000	10.0440
1.5000	10.2440	4.0000	10.0320
1.6000	10.2320	4.2000	10.0200
1.7000	10.2160	4.4000	10.0120
1.8000	10.2040	4.6000	10.0040
1.9000	10.1960	4.8000	9.9920
2.0000	10.1800		

EXPERIMENT NO. 22C

NAHCO3 = 0.9850E-03 NAOH = 0.9850E-03 CACL2 = 0.9950E-03

TEMPERATURE = 25.8 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.2000	10.3894	2.7000	10.1566
0.3000	10.3750	2.8000	10.1494
6.4000	10.3622	2.9000	10.1446
0.5000	10.3502	3.0000	10.1398
0.6000	10.3366	3.1000	10.1350
0.7000	10.3246	3.2000	10.1310
0.8000	10.3134	3.3000	10.1262
0.9000	10.3006	3.4000	10.1222
1.0000	10.2918	3.5000	10.1190
1.1000	10.2806	3.6000	10.1126
1.2000	10.2702	3.7000	10.1086
1.3000	10.2614	3.8000	10.1038
1.4000	10.2518	3.9000	10.0974
1.5000	10.2422	4.0000	10.0942
1.6000	10.2342	4.1000	10.0878
1.7000	10.2262	4.2000	10.0846
1.8000	10.2174	4.3000	10.0806
1.9000	10.2094	4.4000	10.0782
2.0000	10.2022	4.5000	10.0750
2.1000	10.1950	4.6000	10.0718
2.2000	10.1870	4.7000	10.0694
2.3000	10.1814	4.8000	10.0654
2.4000	10.1742	4.9000	10.0614
2.5000	10.1670		
2.6000	10.1614		

EXPERIMENT NO. 23C

NAHCO3 = 0.9850E-03 NAOH = C.7880E-03 CACL2 = 0.9950E-03

TEMPERATURE = 25.1 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 502.

TIME	PH	TIME	PH
0.2000	10.2056	2.7000	9.8488
0.3000	10.1848	2.8000	9.8408
0.4000	10.1672	2.9000	9.8312
0.5000	10.1472	3.0000	9.8216
0.6000	10.1304	3.1000	9.8128
0.7000	10.1136	3.2000	9.8024
0.8000	10.0952	3.3000	9.7936
0.9000	10.0792	3.4000	9.7848
1.0000	10.0632	3.5000	9.7776
1.1000	10.0472	3.6000	9.7672
1.2000	10.0336	3.7000	9.7592
1.3000	10.0192	3.8000	9.7512
1.4000	10.0032	3.9000	9.7424
1.5000	9.9912	4.0000	9.7352
1.6000	9.9776	4.1000	9.7272
1.7000	9.9648	4.2000	9.7192
1.8000	9.9504	4.3000	9.7128
1.9000	9.9376	4.4000	9.7048
2.0000	9.9256	4.5000	9.6992
2.1000	9.9144	4.6000	9.6936
2.2000	9.9032	4.7000	9.6872
2.3000	9.8872	4.8000	9.6824
2.4000	9.8792	4.9000	9.6776
2.5000	9.8696		
2.6000	9.8592		

EXPERIMENT NO. 24C

NAHCO3 = 0.9850E-03 NAOH = 0.5910E-03 CACL2 = 0.9950E-03

TEMPERATURE = 25.0 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 524.

TIME	PH	TIME	PH
0.2000	9.9730	2.7000	9.5034
0.3000	9.9490	2.8000	9.4882
0.4000	9.9274	2.9000	9.4730
0.5000	9.9034	3.0000	9.4610
0.6000	9.8794	3.1000	9.4450
0.7000	9.8602	3.2000	9.4354
0.8000	9.8378	3.3000	9.4210
0.9000	9.8170	3.4000	9.4090
1.0000	9.7970	3.5000	9.3970
1.1000	9.7762	3.6000	9.3850
1.2000	9.7594	3.7000	9.3730
1.3000	9.7394	3.8000	9.3626
1.4000	9.7210	3.9000	9.3514
1.5000	9.7010	4.0000	9.3410
1.6000	9.6826	4.1000	9.3298
1.7000	9.6666	4.2000	9.3178
1.8000	9.6482	4.3000	9.3090
1.9000	9.6290	4.4000	9.2586
2.0000	9.6122	4.5000	9.2882
2.1000	9.5930	4.6000	9.2786
2.2000	9.5786	4.7000	9.2690
2.3000	9.5618	4.8000	9.2578
2.4000	9.5482	4.9000	9.2490
2.5000	9.5298		
2.6000	9.5162		

EXPERIMENT NO. 25C

NAHCO3 = 0.9850E-03 NAOH = 0.3940E-03 CACL2 = 0.9950E-03

TEMPERATURE = 25.5 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 503.

TIME	PH	TIME	PH
0.2000	9.6822	2.6000	9.1182
0.3000	9.6518	2.7000	9.1006
0.4000	9.6222	2.8000	9.0862
0.5000	9.5934	2.9000	9.0694
0.6000	9.5646	3.0000	9.0542
0.7000	9.5366	3.1000	9.0382
0.8000	9.5086	3.2000	9.0222
0.9000	9.4830	3.3000	9.0070
1.0000	9.4574	3.4000	8.9918
1.1000	9.4342	3.5000	8.9782
1.2000	9.4086	3.6000	8.9646
1.3000	9.3846	3.7000	8.9502
1.4000	9.3614	3.8000	8.9366
1.5000	9.3382	3.9000	8.9230
1.6000	9.3182	4.0000	8.9102
1.7000	9.2982	4.1000	8.8982
1.8000	9.2742	4.2000	8.8854
1.9000	9.2542	4.3000	8.8726
2.0000	9.2326	4.4000	8.8622
2.1000	9.2126	4.5000	8.8526
2.2000	9.1926	4.6000	8.8438
2.3000	9.1718	4.7000	8.8326
2.4000	9.1534	4.8000	8.8230
2.5000	9.1358	4.9000	8.8150

EXPERIMENT NO. 26C

NAHCO3 = 0.9850E-03 NAOH = 0.1970E-03 CACL2 = 0.9950E-03

TEMPERATURE = 25.5 DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.2000	9.2926	2.6000	8.8046
0.3000	9.2710	2.7000	8.7886
0.4000	9.2486	2.8000	8.7750
0.5000	9.2254	2.9000	8.7590
0.6000	9.2030	3.0000	8.7430
0.7000	9.1830	3.1000	8.7294
0.8000	9.1590	3.2000	8.7150
0.9000	9.1358	3.3000	8.7014
1.0000	9.1142	3.4000	8.6878
1.1000	9.0926	3.5000	8.6734
1.2000	9.0710	3.6000	8.6598
1.3000	9.0502	3.7000	8.6486
1.4000	9.0294	3.8000	8.6334
1.5000	9.0094	3.9000	8.6214
1.6000	8.9894	4.0000	8.6110
1.7000	8.9710	4.1000	8.5974
1.8000	8.9510	4.2000	8.5870
1.9000	8.9326	4.3000	8.5750
2.0000	8.9126	4.4000	8.5670
2.1000	8.8934	4.5000	8.5550
2.2000	8.8750	4.6000	8.5430
2.3000	8.8566	4.7000	8.5318
2.4000	8.8374	4.8000	8.5222
2.5000	8.8222	4.9000	8.5118

EXPERIMENT NO. 1

NAHCO3 = 0.1561E-02 NAOH = 0.6900E-03 CACL2 = 0.1193E-02

TEMPERATURE = 0.1060E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 4[illegible]

TIME	PH	TIME	PH	TIME	PH
[illegible]	0.9850	[illegible]	0.9650	[illegible]	0.9350
[illegible]	0.9800	[illegible]	0.9600	[illegible]	0.9300
[illegible]	0.9750	[illegible]	0.9550	[illegible]	0.9250
[illegible]	0.9700	[illegible]	0.9500	[illegible]	0.9200
[illegible]	0.9650	[illegible]	0.9450	[illegible]	0.9150
[illegible]	0.9600	[illegible]	0.9400	[illegible]	0.9100
[illegible]	0.9550	[illegible]	0.9350	[illegible]	0.9050
[illegible]	0.9500	[illegible]	0.9300	[illegible]	0.9000
[illegible]	0.9450	[illegible]	0.9250	[illegible]	0.8950
[illegible]	0.9400	[illegible]	0.9200	[illegible]	0.8900
[illegible]	0.9350	[illegible]	0.9150	[illegible]	0.8850
[illegible]	0.9300	[illegible]	0.9100	[illegible]	0.8800
[illegible]	0.9250	[illegible]	0.9050	[illegible]	0.8750
[illegible]	0.9200	[illegible]	0.9000	[illegible]	0.8700
[illegible]	0.9150	[illegible]	0.8950	[illegible]	0.8650
[illegible]	0.9100	[illegible]	0.8900	[illegible]	0.8600
[illegible]	0.9050	[illegible]	0.8850	[illegible]	0.8550
[illegible]	0.9000	[illegible]	0.8800	[illegible]	0.8500
[illegible]	0.8950	[illegible]	0.8750	[illegible]	0.8450
[illegible]	0.8900	[illegible]	0.8700	[illegible]	0.8400
[illegible]	0.8850	[illegible]	0.8650	[illegible]	0.8350
[illegible]	0.8800	[illegible]	0.8600	[illegible]	0.8300
[illegible]	0.8750	[illegible]	0.8550	[illegible]	0.8250
[illegible]	0.8700	[illegible]	0.8500	[illegible]	0.8200
[illegible]	0.8650	[illegible]	0.8450	[illegible]	0.8150
[illegible]	0.8600	[illegible]	0.8400	[illegible]	0.8100
[illegible]	0.8550	[illegible]	0.8350	[illegible]	0.8050
[illegible]	0.8500	[illegible]	0.8300	[illegible]	0.8000
[illegible]	0.8450	[illegible]	0.8250	[illegible]	0.7950
[illegible]	0.8400	[illegible]	0.8200	[illegible]	0.7900
[illegible]	0.8350	[illegible]	0.8150	[illegible]	0.7850
[illegible]	0.8300	[illegible]	0.8100	[illegible]	0.7800
[illegible]	0.8250	[illegible]	0.8050	[illegible]	0.7750
[illegible]	0.8200	[illegible]	0.8000	[illegible]	0.7700
[illegible]	0.8150	[illegible]	0.7950	[illegible]	0.7650
[illegible]	0.8100	[illegible]	0.7900	[illegible]	0.7600
[illegible]	0.8050	[illegible]	0.7850	[illegible]	0.7550
[illegible]	0.8000	[illegible]	0.7800	[illegible]	0.7500
[illegible]	0.7950	[illegible]	0.7750	[illegible]	0.7450
[illegible]	0.7900	[illegible]	0.7700	[illegible]	0.7400
[illegible]	0.7850	[illegible]	0.7650	[illegible]	0.7350
[illegible]	0.7800	[illegible]	0.7600	[illegible]	0.7300
[illegible]	0.7750	[illegible]	0.7550	[illegible]	0.7250
[illegible]	0.7700	[illegible]	0.7500	[illegible]	0.7200
[illegible]	0.7650	[illegible]	0.7450	[illegible]	0.7150
[illegible]	0.7600	[illegible]	0.7400	[illegible]	0.7100
[illegible]	0.7550	[illegible]	0.7350	[illegible]	0.7050
[illegible]	0.7500	[illegible]	0.7300	[illegible]	0.7000
[illegible]	0.7450	[illegible]	0.7250	[illegible]	0.6950
[illegible]	0.7400	[illegible]	0.7200	[illegible]	0.6900
[illegible]	0.7350	[illegible]	0.7150	[illegible]	0.6850
[illegible]	0.7300	[illegible]	0.7100	[illegible]	0.6800
[illegible]	0.7250	[illegible]	0.7050	[illegible]	0.6750
[illegible]	0.7200	[illegible]	0.7000	[illegible]	0.6700
[illegible]	0.7150	[illegible]	0.6950	[illegible]	0.6650
[illegible]	0.7100	[illegible]	0.6900	[illegible]	0.6600
[illegible]	0.7050	[illegible]	0.6850	[illegible]	0.6550
[illegible]	0.7000	[illegible]	0.6800	[illegible]	0.6500
[illegible]	0.6950	[illegible]	0.6750	[illegible]	0.6450
[illegible]	0.6900	[illegible]	0.6700	[illegible]	0.6400
[illegible]	0.6850	[illegible]	0.6650	[illegible]	0.6350
[illegible]	0.6800	[illegible]	0.6600	[illegible]	0.6300
[illegible]	0.6750	[illegible]	0.6550	[illegible]	0.6250
[illegible]	0.6700	[illegible]	0.6500	[illegible]	0.6200
[illegible]	0.6650	[illegible]	0.6450	[illegible]	0.6150
[illegible]	0.6600	[illegible]	0.6400	[illegible]	0.6100
[illegible]	0.6550	[illegible]	0.6350	[illegible]	0.6050
[illegible]	0.6500	[illegible]	0.6300	[illegible]	0.6000
[illegible]	0.6450	[illegible]	0.6250	[illegible]	0.5950
[illegible]	0.6400	[illegible]	0.6200	[illegible]	0.5900
[illegible]	0.6350	[illegible]	0.6150	[illegible]	0.5850
[illegible]	0.6300	[illegible]	0.6100	[illegible]	0.5800
[illegible]	0.6250	[illegible]	0.6050	[illegible]	0.5750
[illegible]	0.6200	[illegible]	0.6000	[illegible]	0.5700
[illegible]	0.6150	[illegible]	0.5950	[illegible]	0.5650
[illegible]	0.6100	[illegible]	0.5900	[illegible]	0.5600
[illegible]	0.6050	[illegible]	0.5850	[illegible]	0.5550
[illegible]	0.6000	[illegible]	0.5800	[illegible]	0.5500
[illegible]	0.5950	[illegible]	0.5750	[illegible]	0.5450
[illegible]	0.5900	[illegible]	0.5700	[illegible]	0.5400
[illegible]	0.5850	[illegible]	0.5650	[illegible]	0.5350
[illegible]	0.5800	[illegible]	0.5600	[illegible]	0.5300
[illegible]	0.5750	[illegible]	0.5550	[illegible]	0.5250
[illegible]	0.5700	[illegible]	0.5500	[illegible]	0.5200
[illegible]	0.5650	[illegible]	0.5450	[illegible]	0.5150
[illegible]	0.5600	[illegible]	0.5400	[illegible]	0.5100
[illegible]	0.5550	[illegible]	0.5350	[illegible]	0.5050
[illegible]	0.5500	[illegible]	0.5300	[illegible]	0.5000
[illegible]	0.5450	[illegible]	0.5250	[illegible]	0.4950
[illegible]	0.5400	[illegible]	0.5200	[illegible]	0.4900
[illegible]	0.5350	[illegible]	0.5150	[illegible]	0.4850
[illegible]	0.5300	[illegible]	0.5100	[illegible]	0.4800
[illegible]	0.5250	[illegible]	0.5050	[illegible]	0.4750
[illegible]	0.5200	[illegible]	0.5000	[illegible]	0.4700
[illegible]	0.5150	[illegible]	0.4950	[illegible]	0.4650
[illegible]	0.5100	[illegible]	0.4900	[illegible]	0.4600
[illegible]	0.5050	[illegible]	0.4850	[illegible]	0.4550
[illegible]	0.5000	[illegible]	0.4800	[illegible]	0.4500
[illegible]	0.4950	[illegible]	0.4750	[illegible]	0.4450
[illegible]	0.4900	[illegible]	0.4700	[illegible]	0.4400
[illegible]	0.4850	[illegible]	0.4650	[illegible]	0.4350
[illegible]	0.4800	[illegible]	0.4600	[illegible]	0.4300
[illegible]	0.4750	[illegible]	0.4550	[illegible]	0.4250
[illegible]	0.4700	[illegible]	0.4500	[illegible]	0.4200
[illegible]	0.4650	[illegible]	0.4450	[illegible]	0.4150
[illegible]	0.4600	[illegible]	0.4400	[illegible]	0.4100
[illegible]	0.4550	[illegible]	0.4350	[illegible]	0.4050
[illegible]	0.4500	[illegible]	0.4300	[illegible]	0.4000
[illegible]	0.4450	[illegible]	0.4250	[illegible]	0.3950
[illegible]	0.4400	[illegible]	0.4200	[illegible]	0.3900
[illegible]	0.4350	[illegible]	0.4150	[illegible]	0.3850
[illegible]	0.4300	[illegible]	0.4100	[illegible]	0.3800
[illegible]	0.4250	[illegible]	0.4050	[illegible]	0.3750
[illegible]	0.4200	[illegible]	0.4000	[illegible]	0.3700
[illegible]	0.4150	[illegible]	0.3950	[illegible]	0.3650
[illegible]	0.4100	[illegible]	0.3900	[illegible]	0.3600
[illegible]	0.4050	[illegible]	0.3850	[illegible]	0.3550
[illegible]	0.4000	[illegible]	0.3800	[illegible]	0.3500
[illegible]	0.3950	[illegible]	0.3750	[illegible]	0.3450
[illegible]	0.3900	[illegible]	0.3700	[illegible]	0.3400
[illegible]	0.3850	[illegible]	0.3650	[illegible]	0.3350
[illegible]	0.3800	[illegible]	0.3600	[illegible]	0.3300
[illegible]	0.3750	[illegible]	0.3550	[illegible]	0.3250
[illegible]	0.3700	[illegible]	0.3500	[illegible]	0.3200
[illegible]	0.3650	[illegible]	0.3450	[illegible]	0.3150
[illegible]	0.3600	[illegible]	0.3400	[illegible]	0.3100
[illegible]	0.3550	[illegible]	0.3350	[illegible]	0.3050
[illegible]	0.3500	[illegible]	0.3300	[illegible]	0.3000
[illegible]	0.3450	[illegible]	0.3250	[illegible]	0.2950
[illegible]	0.3400	[illegible]	0.3200	[illegible]	0.2900
[illegible]	0.3350	[illegible]	0.3150	[illegible]	0.2850
[illegible]	0.3300	[illegible]	0.3100	[illegible]	0.2800
[illegible]	0.3250	[illegible]	0.3050	[illegible]	0.2750
[illegible]	0.3200	[illegible]	0.3000	[illegible]	0.2700
[illegible]	0.3150	[illegible]	0.2950	[illegible]	0.2650
[illegible]	0.3100	[illegible]	0.2900	[illegible]	0.2600
[illegible]	0.3050	[illegible]	0.2850	[illegible]	0.2550
[illegible]	0.3000	[illegible]	0.2800	[illegible]	0.2500
[illegible]	0.2950	[illegible]	0.2750	[illegible]	0.2450
[illegible]	0.2900	[illegible]	0.2700	[illegible]	0.2400
[illegible]	0.2850	[illegible]	0.2650	[illegible]	0.2350
[illegible]	0.2800	[illegible]	0.2600	[illegible]	0.2300
[illegible]	0.2750	[illegible]	0.2550	[illegible]	0.2250
[illegible]	0.2700	[illegible]	0.2500	[illegible]	0.2200
[illegible]	0.2650	[illegible]	0.2450	[illegible]	0.2150
[illegible]	0.2600	[illegible]	0.2400	[illegible]	0.2100
[illegible]	0.2550	[illegible]	0.2350	[illegible]	0.2050
[illegible]	0.2500	[illegible]	0.2300	[illegible]	0.2000
[illegible]	0.2450	[illegible]	0.2250	[illegible]	0.1950
[illegible]	0.2400	[illegible]	0.2200	[illegible]	0.1900
[illegible]	0.2350	[illegible]	0.2150	[illegible]	0.1850
[illegible]	0.2300	[illegible]	0.2100	[illegible]	0.1800
[illegible]	0.2250	[illegible]	0.2050	[illegible]	0.1750
[illegible]	0.2200	[illegible]	0.2000	[illegible]	0.1700
[illegible]	0.2150	[illegible]	0.1950	[illegible]	0.1650
[illegible]	0.2100	[illegible]	0.1900	[illegible]	0.1600
[illegible]	0.2050	[illegible]	0.1850	[illegible]	0.1550
[illegible]	0.2000	[illegible]	0.1800	[illegible]	0.1500
[illegible]	0.1950	[illegible]	0.1750	[illegible]	0.1450
[illegible]	0.1900	[illegible]	0.1700	[illegible]	0.1400
[illegible]	0.1850	[illegible]	0.1650	[illegible]	0.1350
[illegible]	0.1800	[illegible]	0.1600	[illegible]	0.1300
[illegible]	0.1750	[illegible]	0.1550	[illegible]	0.1250
[illegible]	0.1700	[illegible]	0.1500	[illegible]	0.1200
[illegible]	0.1650	[illegible]	0.1450	[illegible]	0.1150
[illegible]	0.1600	[illegible]	0.1400	[illegible]	0.1100
[illegible]	0.1550	[illegible]	0.1350	[illegible]	0.1050
[illegible]	0.1500	[illegible]	0.1300	[illegible]	0.1000
[illegible]	0.1450	[illegible]	0.1250	[illegible]	0.0950
[illegible]	0.1400	[illegible]	0.1200	[illegible]	0.0900
[illegible]	0.1350	[illegible]	0.1150	[illegible]	0.0850
[illegible]	0.1300	[illegible]	0.1100	[illegible]	0.0800
[illegible]	0.1250	[illegible]	0.1050	[illegible]	0.0750
[illegible]	0.1200	[illegible]	0.1000	[illegible]	0.0700
[illegible]	0.1150	[illegible]	0.0950	[illegible]	0.0650
[illegible]	0.1100	[illegible]	0.0900	[illegible]	0.0600
[illegible]	0.1050	[illegible]	0.0850	[illegible]	0.0550
[illegible]	0.1000	[illegible]	0.0800	[illegible]	0.0500
[illegible]	0.0950	[illegible]	0.0750	[illegible]	0.0450
[illegible]	0.0900	[illegible]	0.0700	[illegible]	0.0400
[illegible]	0.0850	[illegible]	0.0650	[illegible]	0.0350
[illegible]	0.0800	[illegible]	0.0600	[illegible]	0.0300
[illegible]	0.0750	[illegible]	0.0550	[illegible]	0.0250
[illegible]	0.0700	[illegible]	0.0500	[illegible]	0.0200
[illegible]	0.0650	[illegible]	0.0450	[illegible]	0.0150
[illegible]	0.0600	[illegible]	0.0400	[illegible]	0.0100
[illegible]	0.0550	[illegible]	0.0350	[illegible]	0.0050
[illegible]	0.0500	[illegible]	0.0300	[illegible]	0.0000

EXPERIMENT NO. 2

NAHCO3 = 0.1561E-02 NAOH = 0.6900E-03 CACL2 = 0.1193E-02

TEMPERATURE = 0.1100E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = [illegible]

TIME	PH	TIME	PH	TIME	PH
[illegible]	0.9850	[illegible]	0.9650	[illegible]	0.9350
[illegible]	0.9800	[illegible]	0.9600	[illegible]	0.9300
[illegible]	0.9750	[illegible]	0.9550	[illegible]	0.9250
[illegible]	0.9700	[illegible]	0.9500	[illegible]	0.9200
[illegible]	0.9650	[illegible]	0.9450	[illegible]	0.9150
[illegible]	0.9600	[illegible]	0.9400	[illegible]	0.9100
[illegible]	0.9550	[illegible]	0.9350	[illegible]	0.9050
[illegible]	0.9500	[illegible]	0.9300	[illegible]	0.9000
[illegible]	0.9450	[illegible]	0.9250	[illegible]	0.8950
[illegible]	0.9400	[illegible]	0.9200	[illegible]	0.8900
[illegible]	0.9350	[illegible]	0.9150	[illegible]	0.8850
[illegible]	0.9300	[illegible]	0.9100	[illegible]	0.8800
[illegible]	0.9250	[illegible]	0.9050	[illegible]	0.8750
[illegible]	0.9200	[illegible]	0.9000	[illegible]	0.8700
[illegible]	0.9150	[illegible]	0.8950	[illegible]	0.8650
[illegible]	0.9100	[illegible]	0.8900	[illegible]	0.8600
[illegible]	0.9050	[illegible]	0.8850	[illegible]	0.8550
[illegible]	0.9000	[illegible]	0.8800	[illegible]	0.8500
[illegible]	0.8950	[illegible]	0.8750	[illegible]	0.8450
[illegible]	0.8900	[illegible]	0.8700	[illegible]	0.8400
[illegible]	0.8850	[illegible]	0.8650	[illegible]	0.8350
[illegible]	0.8800	[illegible]	0.8600	[illegible]	0.8300
[illegible]	0.8750	[illegible]	0.8550	[illegible]	0.8250
[illegible]	0.8700	[illegible]	0.8500	[illegible]	0.8200
[illegible]	0.8650	[illegible]	0.8450	[illegible]	0.8150
[illegible]	0.8600	[illegible]	0.8400	[illegible]	0.8100
[illegible]	0.8550	[illegible]	0.8350	[illegible]	0.8050
[illegible]	0.8500	[illegible]	0.8300	[illegible]	0.8000
[illegible]	0.8450	[illegible]	0.8250	[illegible]	0.7950
[illegible]	0.8400	[illegible]	0.8200	[illegible]	0.7900
[illegible]	0.8350	[illegible]	0.8150	[illegible]	0.7850
[illegible]	0.8300	[illegible]	0.8100	[illegible]	0.7800
[illegible]	0.8250	[illegible]	0.8050	[illegible]	0.7750
[illegible]	0.8200	[illegible]	0.8000	[illegible]	0.7700
[illegible]	0.8150	[illegible]	0.7950	[illegible]	0.7650
[illegible]	0.8100	[illegible]	0.7900	[illegible]	0.7600
[illegible]	0.8050	[illegible]	0.7850	[illegible]	0.7550
[illegible]	0.8000	[illegible]	0.7800	[illegible]	0.7500
[illegible]	0.7950	[illegible]	0.7750	[illegible]	0.7450
[illegible]	0.7900	[illegible]	0.7700	[illegible]	0.7400
[illegible]	0.7850	[illegible]	0.7650	[illegible]	0.7350
[illegible]	0.7800	[illegible]	0.7600	[illegible]	0.7300
[illegible]	0.7750	[illegible]	0.7550	[illegible]	0.7250
[illegible]	0.7700	[illegible]	0.7500	[illegible]	0.7200
[illegible]	0.7650	[illegible]	0.7450	[illegible]	0.7150
[illegible]	0.7600	[illegible]	0.7400	[illegible]	0.7100
[illegible]	0.7550	[illegible]	0.7350	[illegible]	0.7050
[illegible]	0.7500	[illegible]	0.7300	[illegible]	0.7000
[illegible]	0.7450	[illegible]	0.7250	[illegible]	0.6950
[illegible]	0.7400	[illegible]	0.7200	[illegible]	0.6900
[illegible]	0.7350	[illegible]	0.7150	[illegible]	0.6850
[illegible]	0.7300	[illegible]	0.7100	[illegible]	0.6800
[illegible]	0.7250	[illegible]	0.7050	[illegible]	0.6750
[illegible]	0.7200	[illegible]	0.7000	[illegible]	0.6700
[illegible]	0.7150	[illegible]	0.6950	[illegible]	0.6650
[illegible]	0.7100	[illegible]	0.6900	[illegible]	0.6600
[illegible]	0.7050	[illegible]	0.6850	[illegible]	0.6550
[illegible]	0.7000	[illegible]	0.6800	[illegible]	0.6500
[illegible]	0.6950	[illegible]	0.6750	[illegible]	0.6450
[illegible]	0.6900	[illegible]	0.6700	[illegible]	0.6400
[illegible]	0.6850	[illegible]	0.6650	[illegible]	0.6350
[illegible]	0.6800	[illegible]	0.6600	[illegible]	0.6300
[illegible]	0.6750	[illegible]	0.6550	[illegible]	0.6250
[illegible]	0.6700	[illegible]	0.6500	[illegible]	0.6200
[illegible]	0.6650	[illegible]	0.6450	[illegible]	0.6150
[illegible]	0.6600	[illegible]	0.6400	[illegible]	0.6100
[illegible]	0.6550	[illegible]	0.6350	[illegible]	0.6050
[illegible]	0.6500	[illegible]	0.6300	[illegible]	0.6000
[illegible]	0.6450	[illegible]	0.6250	[illegible]	0.5950
[illegible]	0.6400	[illegible]	0.6200	[illegible]	0.5900
[illegible]	0.6350	[illegible]	0.6150	[illegible]	0.5850
[illegible]	0.6300	[illegible]	0.6100	[illegible]	0.5800
[illegible]	0.6250	[illegible]	0.6050	[illegible]	0.5750
[illegible]	0.6200	[illegible]	0.6000	[illegible]	0.5700
[illegible]	0.6150	[illegible]	0.5950	[illegible]	0.5650
[illegible]	0.6100	[illegible]	0.5900	[illegible]	0.5600
[illegible]	0.6050	[illegible]	0.5850	[illegible]	0.5550
[illegible]	0.6000	[illegible]	0.5800	[illegible]	0.5500
[illegible]	0.5950	[illegible]	0.5750	[illegible]	0.5450
[illegible]	0.5900	[illegible]	0.5700	[illegible]	0.5400
[illegible]	0.5850	[illegible]	0.5650	[illegible]	0.5350
[illegible]	0.5800	[illegible]	0.5600	[illegible]	0.5300
[illegible]	0.5750	[illegible]	0.5550	[illegible]	0.5250
[illegible]	0.5700	[illegible]	0.5500	[illegible]	0.5200
[illegible]	0.5650	[illegible]	0.5450	[illegible]	0.5150
[illegible]	0.5600	[illegible]	0.5400	[illegible]	0.5100
[illegible]	0.5550	[illegible]	0.5350	[illegible]	0.5050
[illegible]	0.5500	[illegible]	0.5300	[illegible]	0.5000
[illegible]	0.5450	[illegible]	0.5250	[illegible]	0.4950
[illegible]	0.5400	[illegible]	0.5200	[illegible]	0.4900
[illegible]	0.5350	[illegible]	0.5150	[illegible]	0.4850
[illegible]	0.5300	[illegible]	0.5100	[illegible]	0.4800
[illegible]	0.5250	[illegible]	0.5050	[illegible]	0.4750
[illegible]	0.5200	[illegible]	0.5000	[illegible]	0.4700
[illegible]	0.5150	[illegible]	0.4950	[illegible]	0.4650
[illegible]	0.5100	[illegible]	0.4900	[illegible]	0.4600
[illegible]	0.5050	[illegible]	0.4850	[illegible]	0.4550
[illegible]	0.5000	[illegible]	0.4800	[illegible]	0.4500
[illegible]	0.4950	[illegible]	0.4750	[illegible]	0.4450
[illegible]	0.4900	[illegible]	0.4700	[illegible]	0.4400
[illegible]	0.4850	[illegible]	0.4650	[illegible]	0.4350
[illegible]	0.4800	[illegible]	0.4600	[illegible]	0.4300
[illegible]	0.4750	[illegible]	0.4550	[illegible]	0.4250
[illegible]	0.4700	[illegible]	0.4500	[illegible]	0.4200
[illegible]	0.4650	[illegible]	0.4450	[illegible]	0.4150
[illegible]	0.4600	[illegible]	0.4400	[illegible]	0.4100
[illegible]	0.4550	[illegible]	0.4350	[illegible]	0.4050
[illegible]	0.4500	[illegible]	0.4300	[illegible]	0.4000
[illegible]	0.4450	[illegible]	0.4250	[illegible]	0.3950
[illegible]	0.4400	[illegible]	0.4200	[illegible]	0.3900
[illegible]	0.4350	[illegible]	0.4150	[illegible]	0.3850
[illegible]	0.4300	[illegible]	0.4100	[illegible]	0.3800
[illegible]	0.4250	[illegible]	0.4050	[illegible]	0.3750
[illegible]	0.4200	[illegible]	0.4000	[illegible]	0.3700
[illegible]	0.4150	[illegible]	0.3950	[illegible]	0.3650
[illegible]	0.4100	[illegible]	0.3900	[illegible]	0.3600
[illegible]	0.4050	[illegible]	0.3850	[illegible]	0.3550
[illegible]	0.4000	[illegible]	0.3800	[illegible]	0.3500
[illegible]	0.3950	[illegible]	0.3750	[illegible]	0.3450
[illegible]	0.3900	[illegible]	0.3700	[illegible]	0.3400
[illegible]	0.3850	[illegible]	0.3650	[illegible]	0.3350
[illegible]	0.3800	[illegible]	0.3600	[illegible]	0.3300
[illegible]	0.3750	[illegible]	0.3550	[illegible]	0.3250
[illegible]	0.3700	[illegible]	0.3500	[illegible]	0.3200
[illegible]	0.3650	[illegible]	0.3450	[illegible]	0.3150
[illegible]	0.3600	[illegible]	0.3400	[illegible]	0.3100
[illegible]	0.3550	[illegible]	0.3350	[illegible]	0.3050
[illegible]	0.3500	[illegible]	0.3300	[illegible]	0.3000
[illegible]	0.3450	[illegible]	0.3250	[illegible]	0.2950
[illegible]	0.3400	[illegible]	0.3200	[illegible]	0.2900
[illegible]	0.3350	[illegible]	0.3150	[illegible]	0.2850
[illegible]	0.3300	[illegible]	0.3100	[illegible]	0.2800
[illegible]	0.3250	[illegible]	0.3050	[illegible]	0.2750
[illegible]	0.3200	[illegible]	0.3000	[illegible]	0.2700
[illegible]	0.3150	[illegible]	0.2950	[illegible]	0.2650
[illegible]	0.3100	[illegible]	0.2900	[illegible]	0.2600
[illegible]	0.3050	[illegible]	0.2850	[illegible]	0.2550
[illegible]	0.3000	[illegible]	0.2800	[illegible]	0.2500
[illegible]	0.2950	[illegible]	0.2750	[illegible]	0.2450
[illegible]	0.2900	[illegible]	0.2700	[illegible]	0.2400
[illegible]	0.2850	[illegible]	0.2650	[illegible]	0.2350
[illegible]	0.2800	[illegible]	0.2600	[illegible]	0.2300
[illegible]	0.2750	[illegible]	0.2550	[illegible]	0.2250
[illegible]	0.2700	[illegible]	0.2500	[illegible]	0.2200
[illegible]	0.2650	[illegible]	0.2450	[illegible]	0.2150
[illegible]	0.2600	[illegible]	0.2400	[illegible]	0.2100
[illegible]	0.2550	[illegible]	0.2350	[illegible]	0.2050
[illegible]	0.2500	[illegible]	0.2300	[illegible]	0.2000
[illegible]	0.2450	[illegible]	0.2250	[illegible]	0.1950
[illegible]	0.2400	[illegible]	0.2200	[illegible]	0.1900
[illegible]	0.2350	[illegible]	0.2150	[illegible]	0.1850
[illegible]	0.2300	[illegible]	0.2100	[illegible]	0.1800
[illegible]	0.2250	[illegible]	0.2050	[illegible]	0.1750
[illegible]	0.2200	[illegible]	0.2000	[illegible]	0.1700
[illegible]	0.2150	[illegible]	0.1950	[illegible]	0.1650
[illegible]	0.2100	[illegible]	0.1900	[illegible]	0.1600
[illegible]	0.2050	[illegible]	0.1850	[illegible]	0.1550
[illegible]	0.2000	[illegible]	0.1800	[illegible]	0.1500
[illegible]	0.1950	[illegible]	0.1750	[illegible]	0.1450
[illegible]	0.1900	[illegible]	0.1700	[illegible]	0.1400
[illegible]	0.1850	[illegible]	0.1650	[illegible]	0.1350
[illegible]	0.1800	[illegible]	0.1600	[illegible]	0.1300
[illegible]	0.1750	[illegible]	0.1550	[illegible]	0.1250
[illegible]	0.1700	[illegible]	0.1500	[illegible]	0.1200
[illegible]	0.1650	[illegible]	0.1450	[illegible]	0.1150
[illegible]	0.1600	[illegible]	0.1400	[illegible]	0.1100
[illegible]	0.1550	[illegible]	0.1350	[illegible]	0.1050
[illegible]	0.1500	[illegible]	0.1300	[illegible]	0.1000
[illegible]	0.1450	[illegible]	0.1250	[illegible]	0.0950
[illegible]	0.1400	[illegible]	0.1200	[illegible]	0.0900
[illegible]	0.1350	[illegible]	0.1150	[illegible]	0.0850
[illegible]	0.1300	[illegible]	0.1100	[illegible]	0.0800
[illegible]	0.1250	[illegible]	0.1050	[illegible]	0.0750
[illegible]	0.1200	[illegible]	0.1000	[illegible]	0.0700
[illegible]	0.1150	[illegible]	0.0950	[illegible]	0.0650
[illegible]	0.1100	[illegible]	0.0900	[illegible]	0.0600
[illegible]	0.1050	[illegible]	0.0850	[illegible]	0.0550
[illegible]	0.1000	[illegible]	0.0800	[illegible]	0.0500
[illegible]	0.0950	[illegible]	0.0750	[illegible]	0.0450
[illegible]	0.0900	[illegible]	0.0700	[illegible]	0.0400
[illegible]	0.0850	[illegible]	0.0650	[illegible]	0.0350
[illegible]	0.0800	[illegible]	0.0600	[illegible]	0.0300
[illegible]	0.0750	[illegible]	0.0550	[illegible]	0.0250
[illegible]	0.0700	[illegible]	0.0500	[illegible]	0.0200
[illegible]	0.0650	[illegible]	0.0450	[illegible]	0.0150
[illegible]	0.0600	[illegible]	0.0400	[illegible]	0.0100
[illegible]	0.0550	[illegible]	0.0350	[illegible]	0.0050
[illegible]	0.0500	[illegible]	0.0300	[illegible]	0.0000

EXPERIMENT NO. 3

NAHCO3 = 0.1560E-02 NAOH = 0.6930E-03 CACL2 = 0.1190E-02

TEMPERATURE = 0.1140E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 600.

TIME	PH	TIME	PH	TIME	PH
0.	9.9800	7.2500	9.1350	14.	8.45
0.2500	9.9300	7.5000	9.1200	14.2500	8.3750
0.5000	9.8750	7.7500	9.1050	14.5000	8.8700
0.7500	9.8300	8.0000	9.0900	14.7500	8.3650
1.0000	9.7900	8.2500	9.0800	15.0000	8.8550
1.2500	9.7500	8.5000	9.0700	15.2500	8.8500
1.5000	9.7230	8.7500	9.0550	15.5000	8.8450
1.7500	9.6850	9.0000	9.0400	15.7500	8.8400
2.0000	9.6530	9.2500	9.0300	16.0000	8.8350
2.2500	9.6130	9.5000	9.0200	16.2500	8.8300
2.5000	9.5850	9.7500	9.0100	16.5000	8.8250
2.7500	9.5500	10.0000	9.0000	16.7500	8.8200
3.0000	9.5200	10.2500	8.9900	17.0000	8.8150
3.2500	9.4900	10.5000	8.9800	17.2500	8.8100
3.5000	9.4600	10.7500	8.9650	17.5000	8.8050
3.7500	9.4300	11.0000	8.9500	17.7500	8.7950
4.0000	9.4000	11.2500	8.9350	18.0000	8.7900
4.2500	9.3700	11.5000	8.9450	18.2500	8.7850
4.5000	9.3600	11.7500	8.9350	18.5000	8.7800
4.7500	9.3300	12.0000	8.9300	18.7500	8.7750
5.0000	9.3100	12.2500	8.9200	19.0000	8.7700
5.2500	9.2900	12.5000	8.9100	19.2500	8.7650
5.5000	9.2650	12.7500	8.9050	19.5000	8.7600
5.7500	9.2450	13.0000	8.9000	19.7500	8.7550
6.0000	9.2250	13.2500	8.8950		
6.2500	9.2050	13.5000	8.8900		
6.5000	9.1900	13.7500	8.8850		
6.7500	9.1700				
7.0000	9.1550				

EXPERIMENT NO. 4

NAHCO3 = 0.1560E-02 NAOH = 0.6930E-03 CACL2 = 0.1190E-02

TEMPERATURE = 0.1140E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH	TIME	PH
1.0000	9.9000	8.2500	9.0300	15.5000	8.8150
1.2500	9.8500	8.5000	9.0150	15.7500	8.8050
1.5000	9.8200	8.7500	9.0050	16.0000	8.7950
1.7500	9.7800	9.0000	8.9950	16.2500	8.7900
2.0000	9.7400	9.2500	8.9850	16.5000	8.7850
2.2500	9.7100	9.5000	8.9750	16.7500	8.7800
2.5000	9.6700	9.7500	8.9700	17.0000	8.7750
2.7500	9.6400	10.0000	8.9600	17.2500	8.7650
3.0000	9.6200	10.2500	8.9550	17.5000	8.7600
3.2500	9.5900	10.5000	8.9450	17.7500	8.7550
3.5000	9.5600	10.7500	8.9400	18.0000	8.7500
3.7500	9.5300	11.0000	8.9350	18.2500	8.7450
4.0000	9.5100	11.2500	8.9250	18.5000	8.7400
4.2500	9.4800	11.5000	8.9150	18.7500	8.7350
4.5000	9.4650	11.7500	8.9100	19.0000	8.7300
4.7500	9.4400	12.0000	8.9050	19.2500	8.7250
5.0000	9.4200	12.2500	8.8950	19.5000	8.7200
5.2500	9.4000	12.5000	8.8900	19.7500	8.7150
5.5000	9.3850	12.7500	8.8850	20.0000	8.7100
5.7500	9.3700	13.0000	8.8750	20.2500	8.7050
6.0000	9.3550	13.2500	8.8700	20.5000	8.7000
6.2500	9.3400	13.5000	8.8650	20.7500	8.6950
6.5000	9.3250	13.7500	8.8600	21.0000	8.6900
6.7500	9.3100	14.0000	8.8550	21.2500	8.6850
7.0000	9.2950	14.2500	8.8500	21.5000	8.6800
7.2500	9.2800	14.5000	8.8450	21.7500	8.6750
7.5000	9.2650	14.7500	8.8400	22.0000	8.6700
7.7500	9.2500	15.0000	8.8350	22.2500	8.6650
8.0000	9.2350	15.2500	8.8300	22.5000	8.6600

EXPERIMENT NO. 5

NAHCO3 = [illegible] NAOH = [illegible] CACL2 = [illegible]

TEMPERATURE = [illegible] DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = [illegible]%

TIME	PH	TIME	PH
[illegible]	[illegible]	[illegible]	[illegible]

EXPERIMENT NO. 6

NAHCO3 = [illegible] NAOH = [illegible] CACL2 = [illegible]

TEMPERATURE = [illegible] DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = [illegible]%

TIME	PH	TIME	PH	TIME	PH
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

EXPERIMENT NO. 7

NAHCO3 = 0.1550E-02 NAOH = 0.6900E-03 CACL2 = 0.1190E-02

TEMPERATURE = 0.2050E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
1.0000	9.8100	8.0000	8.3600
1.2500	9.7500	8.2500	8.3500
1.5000	9.7000	8.5000	8.3350
1.7500	9.6500	8.7500	8.3250
2.0000	9.6000	9.0000	8.3100
2.2500	9.5550	9.2500	8.3000
2.5000	9.5200	9.5000	8.2900
2.7500	9.4800	9.7500	8.2800
3.0000	9.4350	10.0000	8.2700
3.2500	9.4000	10.2500	8.2650
3.5000	9.3650	10.5000	8.2550
3.7500	9.3300	10.7500	8.2450
4.0000	9.3000	11.0000	8.2350
4.2500	9.2700	11.2500	8.2300
4.5000	9.2450	11.5000	8.2250
4.7500	9.2100	11.7500	8.2150
5.0000	9.1850	12.0000	8.2100
5.2500	9.1700	12.2500	8.2000
5.5000	9.1400	12.5000	8.1950
5.7500	9.1200	12.7500	8.1900
6.0000	9.1000	13.0000	8.1850
6.2500	9.0800	13.2500	8.1800
6.5000	9.0600	13.5000	8.1750
6.7500	9.0400	13.7500	8.1700
7.0000	9.0250	14.0000	8.1650
7.2500	9.0050	14.2500	8.1600
7.5000	8.9950	14.5000	8.1550
7.7500	8.9800	14.7500	8.1500

EXPERIMENT NO. 8

NAHCO3 = 0.1550E- 2 NAOH = 0.6900E-03 CACL2 = 0.1190E-02

TEMPERATURE = 0.2040E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 600.

TIME	PH	TIME	PH
1.0000	9.7700	7.7500	8.8800
1.2500	9.7050	8.0000	8.8700
1.5000	9.6450	8.2500	8.8600
1.7500	9.5850	8.5000	8.8450
2.0000	9.5350	8.7500	8.8350
2.2500	9.4900	9.0000	8.8300
2.5000	9.4400	9.2500	8.8200
2.7500	9.3950	9.5000	8.8100
3.0000	9.3500	9.7500	8.8000
3.2500	9.3100	10.0000	8.7900
3.5000	9.2800	10.2500	8.7800
3.7500	9.2400	10.5000	8.7750
4.0000	9.2000	10.7500	8.7700
4.2500	9.1700	11.0000	8.7650
4.5000	9.1450	11.2500	8.7550
4.7500	9.1200	11.5000	8.7500
5.0000	9.0950	11.7500	8.7450
5.2500	9.0700	12.0000	8.7400
5.5000	9.0450	12.2500	8.7350
5.7500	9.0200	12.5000	8.7300
6.0000	9.0000	12.7500	8.7250
6.2500	8.9800	13.0000	8.7200
6.5000	8.9600	13.2500	8.7150
6.7500	8.9400	13.5000	8.7100
7.0000	8.9250	13.7500	8.7050
7.2500	8.9100	14.0000	8.7000
7.5000	8.8950	14.2500	8.6950
7.7500	8.8800	14.5000	8.6900
		14.7500	8.6850

EXPERIMENT NO. 9

NAHCO3 = 0.1550E-02 NAOH = 0.6900E-03 CACL2 = 0.1190E-02

TEMPERATURE = 0.2080E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH	TIME	PH
0.7500	9.8150	4.2500	9.1000	7.7500	8.8350
0.8750	9.7750	4.3750	9.0900	7.8750	8.8300
1.0000	9.7400	4.5000	9.0750	8.0000	8.8250
1.1250	9.7100	4.6250	9.0650	8.1250	8.8200
1.2500	9.6700	4.7500	9.0500	8.2500	8.8150
1.3750	9.6350	4.8750	9.0350	8.2750	8.8100
1.5000	9.6000	5.0000	9.0200	8.3000	8.8050
1.6250	9.5700	5.1250	9.0100	8.3250	8.8000
1.7500	9.5400	5.2500	9.0000	8.3500	8.7950
1.8750	9.5100	5.3750	8.9700	8.3750	8.7900
2.0000	9.4900	5.5000	8.9650	8.4000	8.7850
2.1250	9.4550	5.6250	8.9600	8.4250	8.7800
2.2500	9.4300	5.7500	8.9550	8.4500	8.7800
2.3750	9.4000	5.8750	8.9450	8.4750	8.7750
2.5000	9.3800	6.0000	8.9400	8.5000	8.7700
2.6250	9.3550	6.1250	8.9250	8.5250	8.7700
2.7500	9.3300	6.2500	8.9200	8.5500	8.7650
2.8750	9.3100	6.3750	8.9100	8.5750	8.7600
3.0000	9.2950	6.5000	8.9000	10.0000	8.7600
3.1250	9.2650	6.6250	8.8900	10.1250	8.7550
3.2500	9.2500	6.7500	8.8850	10.2500	8.7550
3.3750	9.2250	6.8750	8.8800	10.3750	8.7500
3.5000	9.2250	7.0000	8.8750	10.5000	8.7500
3.6250	9.1900	7.1250	8.8650	10.6250	8.7450
3.7500	9.1700	7.2500	8.8550	10.7500	8.7450
3.8750	9.1500	7.3750	8.8500	10.8750	8.7400
4.0000	9.1350	7.5000	8.8450		
4.1250	9.1150	7.6250	8.8400		

EXPERIMENT NO. 10

NAHCO3 = 0.1550E-02 NAOH = 0.6900E-03 CACL2 = 0.1190E-02

TEMPERATURE = 0.2080E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 800.

TIME	PH	TIME	PH	TIME	PH
0.5000	9.8700	4.1250	9.0500	7.3750	8.7850
0.6250	9.8300	4.2500	9.0300	7.5000	8.7800
0.7500	9.7800	4.3750	9.0200	7.6250	8.7750
0.8750	9.7350	4.5000	9.0050	7.7500	8.7700
1.0000	9.7100	4.6250	8.9900	7.8750	8.7650
1.1250	9.6550	4.7500	8.9800	8.0000	8.7600
1.2500	9.6100	4.8750	8.9650	8.1250	8.7600
1.3750	9.5800	5.0000	8.9500	8.2500	8.7550
1.5000	9.5500	5.1250	8.9400	8.3750	8.7550
1.6250	9.5100	5.2500	8.9250	8.5000	8.7500
1.7500	9.4800	5.3750	8.9200	8.6250	8.7500
1.8750	9.4600	5.5000	8.9100	8.7500	8.7450
2.0000	9.4200	5.6250	8.9000	9.1250	8.7400
2.1250	9.3900	5.7500	8.8900	9.2500	8.7400
2.2500	9.3600	5.8750	8.8800	9.3750	8.7350
2.3750	9.3350	6.0000	8.8700	9.5000	8.7300
2.5000	9.3150	6.1250	8.8550	9.6250	8.7300
2.6250	9.2900	6.2500	8.8600	9.7500	8.7300
2.7500	9.2600	6.3750	8.8500	9.8750	8.7250
2.8750	9.2400	6.5000	8.8450	10.0000	8.7250
3.0000	9.2150	6.6250	8.8400	10.1250	8.7200
3.1250	9.1900	6.7500	8.8350	10.2500	8.7200
3.2500	9.1750	6.8750	8.8250	10.3750	8.7150
3.3750	9.1500	7.0000	8.8150	10.5000	8.7150
3.5000	9.1300	7.1250	8.8100	10.6250	8.7100
3.6250	9.1100	7.2500	8.8050	10.7500	8.7100
3.7500	9.0900	7.3750	8.8000	10.8750	8.7100
3.8750	9.0750	7.5000	8.7950		
4.0000	9.0600	7.6250	8.7900		

EXPERIMENT NO. 11

NAHCO3 = 0.1570E-02 NAOH = 0.6650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.2970E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 400.

TIME	PH	TIME	PH	TIME	PH
0.8330	9.7200	3.2500	9.2250	5.0000	8.8750
0.9170	9.6950	3.3330	9.1900	5.0830	8.8650
1.0000	9.6750	3.4160	9.1800	5.1670	8.8450
1.0830	9.6550	3.5000	9.1700	5.2500	8.8350
1.1670	9.6300	3.5830	9.1600	5.3330	8.8250
1.2500	9.6100	3.6670	9.1450	5.4160	8.8150
1.3330	9.5900	3.7500	9.1350	5.5000	8.8050
1.4160	9.5650	3.8330	9.1250	5.5830	8.7950
1.5000	9.5450	3.9170	9.1150	5.6670	8.7850
1.5830	9.5300	4.0000	9.1050	5.7500	8.7750
1.6670	9.5050	4.0830	9.0950	5.8330	8.7650
1.7500	9.4800	4.1670	9.0850	5.9170	8.7550
1.8330	9.4700	4.2500	9.0750	6.0000	8.7450
1.9170	9.4450	4.3330	9.0650	6.0830	8.7350
2.0000	9.4350	4.4160	9.0550	6.1670	8.7250
2.0830	9.4100	4.5000	9.0450	6.2500	8.7150
2.1670	9.3950	4.5830	9.0350	6.3330	8.7050
2.2500	9.3700	4.6670	9.0300	6.4170	8.6950
2.3330	9.3650	4.7500	9.0200	6.5000	8.6850
2.4160	9.3500	4.8330	9.0100	6.5830	8.6750
2.5000	9.3350	4.9170	9.0000	6.6670	8.6650
2.5830	9.3250	5.0000	8.9950	6.7500	8.6550
2.6670	9.3050	5.0830	8.9850	6.8330	8.6450
2.7500	9.2950	5.1670	8.9800	6.9170	8.6350
2.8330	9.2750	5.2500	8.9700	7.0000	8.6250
2.9170	9.2650	5.3330	8.9650	7.0830	8.6150
3.0000	9.2500	5.4160	8.9600	7.1670	8.6050
3.0830	9.2350			7.2500	8.5950
3.1670	9.2200			7.3330	8.5850
				7.4160	8.5750

EXPERIMENT NO. 12

NAHCO3 = 0.1570E-02 NAOH = 0.6650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.2915E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH	TIME	PH
0.6670	9.7150	2.0833	9.1400	4.9170	8.8750
0.7500	9.6800	2.1670	9.1250	5.0000	8.8650
0.8330	9.6550	2.2500	9.1100	5.0830	8.8550
0.9170	9.6250	2.3330	9.0950	5.1670	8.8450
1.0000	9.5900	2.4160	9.0850	5.2500	8.8350
1.0830	9.5700	2.5000	9.0700	5.3330	8.8250
1.1670	9.5400	2.5830	9.0600	5.4160	8.8150
1.2500	9.5150	2.6670	9.0450	5.5000	8.8050
1.3330	9.4950	2.7500	9.0300	5.5830	8.7950
1.4160	9.4650	2.8330	9.0200	5.6670	8.7850
1.5000	9.4450	2.9170	9.0100	5.7500	8.7750
1.5830	9.4250	3.0000	8.9950	5.8330	8.7650
1.6670	9.4000	3.0830	8.9850	5.9170	8.7550
1.7500	9.3750	3.1670	8.9750	6.0000	8.7450
1.8330	9.3600	3.2500	8.9650	6.0830	8.7350
1.9170	9.3350	3.3330	8.9550	6.1670	8.7250
2.0000	9.3150	3.4160	8.9450	6.2500	8.7150
2.0830	9.2950	3.5000	8.9350	6.3330	8.7050
2.1670	9.2800	3.5830	8.9250	6.4160	8.6950
2.2500	9.2650	3.6670	8.9150	6.5000	8.6850
2.3330	9.2450	3.7500	8.9050	6.5830	8.6750
2.4160	9.2250	3.8330	8.8950	6.6670	8.6650
2.5000	9.2150	3.9170	8.8850	6.7500	8.6550
2.5830	9.2000	4.0000	8.8750	6.8330	8.6450
2.6670	9.1750	4.0830	8.8650	6.9170	8.6350
2.7500	9.1550	4.1670	8.8550	7.0000	8.6250
		4.2500	8.8450	7.0830	8.6150
		4.3330	8.8350	7.1670	8.6050
		4.4160	8.8250	7.2500	8.5950
		4.5000	8.8150	7.3330	8.5850
		4.5830	8.8050	7.4160	8.5750
		4.6670	8.7950		
		4.7500	8.7850		
		4.8330	8.7750		
		4.9170	8.7650		
		5.0000	8.7550		
		5.0830	8.7450		
		5.1670	8.7350		
		5.2500	8.7250		
		5.3330	8.7150		
		5.4160	8.7050		

EXPERIMENT NO. 13

NAHCO3 = 0.1570E-02 NAOH = 0.6650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.2900E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 600.

TIME	PH	TIME	PH	TIME	PH
0.5830	9.7050	2.7500	9.0800	4.8330	8.8150
0.6670	9.6700	2.8330	9.0650	4.9170	8.8050
0.7500	9.6400	2.9170	9.0450	5.0000	8.8000
0.8330	9.6100	3.0000	9.0300	5.0830	8.7900
0.9170	9.5750	3.0830	9.0200	5.1670	8.7850
1.0000	9.5400	3.1670	9.0050	5.2500	8.7800
1.0830	9.5100	3.2500	8.9900	5.3330	8.7750
1.1670	9.4800	3.3330	8.9800	5.4160	8.7700
1.2500	9.4600	3.4160	8.9650	5.5000	8.7650
1.3330	9.4300	3.5000	8.9550	5.5830	8.7600
1.4160	9.4000	3.5830	8.9400	5.6670	8.7500
1.5000	9.3800	3.6670	8.9300	5.7500	8.7450
1.5830	9.3500	3.7500	8.9250	5.8330	8.7450
1.6670	9.3350	3.8330	8.9100	5.9170	8.7400
1.7500	9.3450	3.9170	8.9000	6.0000	8.7350
1.8330	9.2800	4.0000	8.8900	6.0830	8.7300
1.9170	9.2600	4.0830	8.8800	6.1670	8.7250
2.0000	9.2450	4.1670	8.8750	6.2500	8.7200
2.0830	9.2200	4.2500	8.8650	6.3330	8.7150
2.1670	9.2000	4.3330	8.8600	6.4160	8.7100
2.2500	9.1350	4.4160	8.8500	6.5000	8.7100
2.3330	9.1670	4.5000	8.8400	6.5830	8.7100
2.4160	9.1400	4.5830	8.8350	6.6670	8.7050
2.5000	9.1250	4.6670	8.8300	6.7500	8.7000
2.5830	9.1100	4.7500	8.8200	6.8330	8.7
2.6670	9.0950			6.9170	8.6950

EXPERIMENT NO. 14

NAHCO3 = 0.1570E-02 NAOH = 0.6650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.2915E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH	TIME	PH
0.5000	9.7900	2.0000	9.2200	3.6670	8.8900
0.5830	9.7500	2.0830	9.1900	3.7500	8.8850
0.6670	9.7100	2.1670	9.1750	3.8330	8.8700
0.7500	9.6650	2.2500	9.1550	3.9170	8.8650
0.8330	9.6300	2.3330	9.1350	4.0000	8.8550
0.9170	9.5900	2.4160	9.1150	4.0830	8.8400
1.0000	9.5500	2.5000	9.0900	4.1670	8.8350
1.0830	9.5250	2.5830	9.0750	4.2500	8.8250
1.1670	9.4900	2.6670	9.0600	4.3330	8.8100
1.2500	9.4600	2.7500	9.0400	4.4160	8.8100
1.3330	9.4300	2.8330	9.0200	4.5000	8.8000
1.4160	9.4100	2.9170	9.0050	4.5830	8.7950
1.5000	9.3700	3.0000	8.9900	4.6670	8.7900
1.5830	9.3400	3.0830	8.9700	4.7500	8.7850
1.6670	9.3150	3.1670	8.9600	4.8330	8.7750
1.7500	9.2900	3.2500	8.9450	4.9170	8.7700
1.8330	9.2600	3.3330	8.9350	5.0000	8.7600
1.9170	9.2400	3.4160	8.9250	5.0830	8.7550
		3.5000	8.9050	5.1670	8.7550
		3.5830	8.9000	5.2500	8.7500
				5.3330	8.7450
				5.4160	8.7400

EXPERIMENT NO. 15

NAHCO3 = 0.1570E-02 NAOH = 0.8650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.2900E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 800.

TIME	PH	TIME	PH	TIME	PH
0.9830	9.7150	2.1670	9.1150	3.7500	8.8350
0.6670	9.6700	2.2500	9.0900	3.8330	8.8250
0.7500	9.6300	2.3330	9.0700	3.9170	8.8200
0.8330	9.5900	2.4160	9.0500	4.0000	8.8150
0.9170	9.5500	2.5000	9.0300	4.0830	8.8000
1.0000	9.5100	2.5830	9.0150	4.1670	8.7900
1.0830	9.4700	2.6670	8.9950	4.2500	8.7850
1.1670	9.4400	2.7500	8.9850	4.3330	8.7800
1.2500	9.4100	2.8330	8.9650	4.4160	8.7700
1.3330	9.3700	2.9170	8.9550	4.5000	8.7650
1.4160	9.3400	3.0000	8.9450	4.5830	8.7600
1.5000	9.3150	3.0830	8.9200	4.6670	8.7550
1.5830	9.2850	3.1670	8.9150	4.7500	8.7500
1.6670	9.2600	3.2500	8.9000	4.8330	8.7450
1.7500	9.2300	3.3330	8.8900	4.9170	8.7400
1.8330	9.2050	3.4160	8.8800	5.0000	8.7350
1.9170	9.1800	3.5000	8.8700	5.0830	8.7300
2.0000	9.1500	3.5830	8.8550	5.1670	8.7250
2.0830	9.1350	3.6670	8.8450		

EXPERIMENT NO. 16

NAHCO3 = 0.1550E-02 NAOH = 0.8650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.2980E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 400.

TIME	PH	TIME	PH
0.6670	9.5850	3.0000	8.8500
0.7500	9.5400	3.0830	8.8350
0.8330	9.5000	3.1670	8.8250
0.9170	9.4750	3.2500	8.8150
1.0000	9.4300	3.3330	8.8000
1.0830	9.3950	3.4160	8.7900
1.1670	9.3600	3.5000	8.7750
1.2500	9.3300	3.5830	8.7650
1.3330	9.2950	3.6670	8.7550
1.4160	9.2650	3.7500	8.7450
1.5000	9.2350	3.8330	8.7300
1.5830	9.2100	3.9170	8.7200
1.6670	9.1800	4.0000	8.7150
1.7500	9.1500	4.0830	8.7050
1.8330	9.1250	4.1670	8.6950
1.9170	9.1050	4.2500	8.6850
2.0000	9.0850	4.3330	8.6800
2.0830	9.0650	4.4160	8.6700
2.1670	9.0350	4.5000	8.6650
2.2500	9.0150	4.5830	8.6550
2.3330	8.9900	4.6670	8.6500
2.4160	8.9700	4.7500	8.6400
2.5000	8.9500	4.8330	8.6400
2.5830	8.9350	4.9170	8.6350
2.6670	8.9150	5.0000	8.6250
2.7500	8.9000	5.0830	8.6150
2.8330	8.8850	5.1670	8.6150
2.9170	8.8700		

EXPERIMENT NO. 17

NAHCO3 = 0.1550E-02 NAOH = 0.6650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.3970E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0

TIME	PH	TIME	PH
0.6670	9.5400	3.0000	8.7850
0.7500	9.4900	3.0830	8.7750
0.8330	9.4500	3.1670	8.7600
0.9170	9.4050	3.2500	8.7500
1.0000	9.3700	3.3330	8.7400
1.0830	9.3250	3.4160	8.7300
1.1670	9.2900	3.5000	8.7200
1.2500	9.2500	3.5830	8.7100
1.3330	9.2150	3.6670	8.7000
1.4160	9.1850	3.7500	8.6950
1.5000	9.1550	2.8330	8.6900
1.5830	9.1200	3.9170	8.6850
1.6670	9.0950	4.0000	8.6750
1.7500	9.0700	4.0830	8.6650
1.8330	9.0450	4.1670	8.6600
1.9170	9.0150	4.2500	8.6550
2.0000	8.9900	4.3330	8.6450
2.0830	8.9700	4.4160	8.6400
2.1670	8.9450	4.5000	8.6350
2.2500	8.9300	4.5830	8.6300
2.3330	8.9100	4.6670	8.6250
2.4160	8.8900	4.7500	8.6200
2.5000	8.8700	4.8330	8.6150
2.5830	8.8550	4.9170	8.6100
2.6670	8.8400	5.0000	8.6050
2.7500	8.8250	5.0830	8.6000
2.8330	8.8100	5.1670	8.5950
2.9170	8.7950	5.2500	8.5900

EXPERIMENT NO. 18

NAHCO3 = 0.1550E-02 NAOH = 0.6650E-03 CACL2 = 0.1180E-02

TEMPERATURE = 0.4000E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.0

TIME	PH	TIME	PH
0.6670	9.5250	2.8330	8.8000
0.7500	9.4800	2.9170	8.7900
0.8330	9.4300	3.0000	8.7750
0.9170	9.3800	3.0830	8.7650
1.0000	9.3300	3.1670	8.7550
1.0830	9.2900	3.2500	8.7500
1.1670	9.2500	3.3330	8.7400
1.2500	9.2100	3.4160	8.7300
1.3330	9.1800	3.5000	8.7200
1.4160	9.1500	3.5830	8.7100
1.5000	9.1200	3.6670	8.7000
1.5830	9.0950	3.7500	8.6950
1.6670	9.0550	3.8330	8.6900
1.7500	9.0300	3.9170	8.6850
1.8330	9.0050	4.0000	8.6800
1.9170	8.9350	4.0830	8.6800
2.0000	8.9600	4.1670	8.6750
2.0830	8.9400	4.2500	8.6700
2.1670	8.9250	4.3330	8.6650
2.2500	8.9050	4.4160	8.6600
2.3330	8.8900	4.5000	8.6550
2.4160	8.8750	4.5830	8.6450
2.5000	8.8550	4.6670	8.6400
2.5830	8.8400	4.7500	8.6400
2.6670	8.8250	4.8330	8.6400
2.7500	8.8150	4.9170	8.6350

EXPERIMENT NO. 19

NAHCO3 = 0.1550E-02 NAOH = 0.6650E-03 CACL2 = 0.1140E-02

TEMPERATURE = 0.3900E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.6670	9.5100	2.7500	8.8700
0.7500	9.4700	2.8330	8.8600
0.8330	9.4250	2.9170	8.8500
0.9170	9.3800	3.0000	8.8200
1.0000	9.3400	3.0830	8.8050
1.0830	9.3050	3.1670	8.8000
1.1670	9.2700	3.2500	8.7850
1.2500	9.2400	3.3330	8.7750
1.3330	9.2100	3.5830	8.7450
1.4160	9.1800	3.6670	8.7350
1.5000	9.1550	3.7500	8.7300
1.5830	9.1250	3.8330	8.7250
1.6670	9.0950	3.9170	8.7200
1.7500	9.0750	4.0000	8.7150
1.8330	9.0500	4.0830	8.7050
1.9170	9.0250	4.1670	8.7000
2.0000	9.0050	4.2500	8.6900
2.0830	8.9900	4.3330	8.6850
2.1670	8.9700	4.4160	8.6850
2.2500	8.9550	4.5000	8.6800
2.3330	8.9400	4.5830	8.6750
2.4160	8.9150	4.6670	8.6700
2.5000	8.9050	4.7500	8.6650
2.5830	8.9000	4.8330	8.6650
2.6670	8.8850		

EXPERIMENT NO. 20

NAHCO3 = 0.1550E-02 NAOH = 0.6650E-03 CACL2 = 0.1140E-02

TEMPERATURE = 0.3900E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 800.

TIME	PH	TIME	PH
0.6670	9.3850	2.5830	8.7250
0.7500	9.3300	2.6670	8.7200
0.8330	9.2800	2.7500	8.7050
0.9170	9.2300	2.8330	8.7000
1.0000	9.1900	2.9170	8.6900
1.0830	9.1450	3.0000	8.6800
1.1670	9.1050	3.0830	8.6750
1.2500	9.0700	3.1670	8.6650
1.3330	9.0300	3.2500	8.6600
1.4160	9.0000	3.3330	8.6500
1.5000	8.9750	3.4160	8.6450
1.5830	8.9450	3.5000	8.6400
1.6670	8.9200	3.5830	8.6350
1.7500	8.8950	3.6670	8.6300
1.8330	8.8700	3.7500	8.6250
1.9170	8.8500	3.8330	8.6200
2.0000	8.8300	3.9170	8.6200
2.0830	8.8100	4.0000	8.6150
2.1670	8.7950	4.0830	8.6100
2.2500	8.7750	4.1670	8.6100
2.3330	8.7650	4.2500	8.6050
2.4160	8.7500	4.3330	8.6000
2.5000	8.7400	4.4160	8.5950

EXPERIMENT NO. 22

NAHCO3 = 0.1140E-02 NAOH = 0.6650E-03 CACL2 = 0.1141E-02

TEMPERATURE = 0.2160E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	10.1350	8.2500	9.1150
0.2500	10.0900	8.5000	9.1050
0.5000	10.0200	8.7500	9.1000
0.7500	9.9650	9.0000	9.0800
1.0000	9.9100	9.2500	9.0650
1.2500	9.8600	9.5000	9.0500
1.5000	9.8100	9.7500	9.0450
1.7500	9.7650	10.0000	9.0300
2.0000	9.7200	10.2500	9.0250
2.2500	9.6800	10.5000	9.0200
2.5000	9.6450	10.7500	9.0100
2.7500	9.6050	11.0000	9.0000
3.0000	9.5700	11.2500	8.9900
3.2500	9.5350	11.5000	8.9850
3.5000	9.5050	11.7500	8.9800
3.7500	9.4750	12.0000	8.9700
4.0000	9.4500	12.2500	8.9650
4.2500	9.4200	12.5000	8.9600
4.5000	9.3900	12.7500	8.9500
4.7500	9.3700	13.0000	8.9450
5.0000	9.3450	13.2500	8.9400
5.2500	9.3200	13.5000	8.9350
5.5000	9.3000	13.7500	8.9300
5.7500	9.2800	14.0000	8.9250
6.0000	9.2600	14.2500	8.9200
6.2500	9.2400	14.5000	8.9150
6.5000	9.2250	14.7500	8.9100
6.7500	9.2000	15.0000	8.9050
7.0000	9.1900	15.2500	8.9000
7.2500	9.1700	15.5000	8.8950
7.5000	9.1550	15.7500	8.8900
7.7500	9.1450	16.0000	8.8850
8.0000	9.1300	16.2500	8.8800

EXPERIMENT NO. 23

NAHCO3 = 0.1710E-02 NAOH = 0.6650E-03 CACL2 = 0.1141E-02

TEMPERATURE = 0.2150E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.7500	9.9600	8.7500	9.0950
1.0000	9.8550	9.0000	9.0850
1.2500	9.8000	9.2500	9.0750
1.5000	9.7500	9.5000	9.0650
1.7500	9.7050	9.7500	9.0550
2.0000	9.6600	10.0000	9.0450
2.2500	9.6200	10.2500	9.0400
2.5000	9.5850	10.5000	9.0300
2.7500	9.5450	10.7500	9.0250
3.0000	9.5100	11.0000	9.0150
3.2500	9.4800	11.2500	9.0100
3.5000	9.4550	11.5000	9.0050
3.7500	9.4200	11.7500	8.9950
4.0000	9.3950	12.0000	8.9900
4.2500	9.3700	12.2500	8.9850
4.5000	9.3500	12.5000	8.9750
4.7500	9.3200	12.7500	8.9700
5.0000	9.3050	13.0000	8.9650
5.2500	9.2800	13.2500	8.9600
5.5000	9.2700	13.5000	8.9550
5.7500	9.2500	13.7500	8.9500
6.0000	9.2350	14.0000	8.9450
6.2500	9.2150	14.2500	8.9400
6.5000	9.2000	14.5000	8.9350
6.7500	9.1850	14.7500	8.9300
7.0000	9.1700	15.0000	8.9300
7.2500	9.1600	15.2500	8.9250
7.5000	9.1450	15.5000	8.9200
7.7500	9.1350	15.7500	8.9200
8.0000	9.1250	16.0000	8.9150
8.2500	9.12	16.2500	8.9100
8.5000	9.1		

EXPERIMENT NO. 24

NAHCO3 = 0.2280E-02 NAOH = 0.6650E-02 CACL2 = 0.1141E-02

TEMPERATURE = 0.2100E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH	TIME	PH
0.0	9.9800	3.8750	9.2250	7.7500	8.8900
0.1250	9.9500	4.0000	9.2100	7.8750	8.8800
0.2500	9.9200	4.1250	9.1900	8.0000	8.8750
0.3750	9.8900	4.2500	9.1800	8.1250	8.8650
0.5000	9.8600	4.3750	9.1650	8.2500	8.8600
0.6250	9.8300	4.5000	9.1500	8.3750	8.8550
0.7500	9.7950	4.6250	9.1350	8.5000	8.8500
0.8750	9.7700	4.7500	9.1250	8.6250	8.8450
1.0000	9.7350	4.8750	9.1150	8.7500	8.8400
1.1250	9.7100	5.0000	9.0950	8.8750	8.8300
1.2500	9.6750	5.1250	9.0850	9.0000	8.8250
1.3750	9.6500	5.2500	9.0700	9.1250	8.8200
1.5000	9.6200	5.3750	9.0600	9.2500	8.8150
1.6250	9.6000	5.5000	9.0500	9.3750	8.8100
1.7500	9.5750	5.6250	9.0400	9.5000	8.8050
1.8750	9.5500	5.7500	9.0300	9.6250	8.8000
2.0000	9.5250	5.8750	9.0200	9.7500	8.7950
2.1250	9.5000	6.0000	9.0100	9.8750	8.7900
2.2500	9.4750	6.1250	9.0000	10.0000	8.7850
2.3750	9.4550	6.2500	8.9850	10.1250	8.7800
2.5000	9.4350	6.3750	8.9750	10.2500	8.7750
2.6250	9.4100	6.5000	8.9700	10.3750	8.7700
2.7500	9.3850	6.6250	8.9600	10.5000	8.7650
2.8750	9.3650	6.7500	8.9500	10.6250	8.7600
3.0000	9.3500	6.8750	8.9400	10.7500	8.7600
3.1250	9.3250	7.0000	8.9300	10.8750	8.7550
3.2500	9.3100	7.1250	8.9250	11.0000	8.7500
3.3750	9.2900	7.2500	8.9200	11.1250	8.7500
3.5000	9.2700	7.3750	8.9100		
3.6250	9.2550	7.5000	8.9000		
3.7500	9.2400	7.6250	8.8950		

EXPERIMENT NO. 27

NAHCO3 = 0.1533E-02 NAOH = 0.6650E-02 CACL2 = 0.8820E-03

TEMPERATURE = 0.2150E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH	TIME	PH
0.0	9.9600	3.7500	9.5100	7.6250	9.3200
0.1250	9.9300	3.8750	9.5050	7.7500	9.3150
0.2500	9.9100	4.0000	9.4950	7.8750	9.3100
0.3750	9.8900	4.1250	9.4850	8.0000	9.3100
0.5000	9.8650	4.2500	9.4800	8.1250	9.3050
0.6250	9.8500	4.3750	9.4700	8.2500	9.3000
0.7500	9.8300	4.5000	9.4600	8.3750	9.3000
0.8750	9.8050	4.6250	9.4550	8.5000	9.2950
1.0000	9.7900	4.7500	9.4500	8.6250	9.2900
1.1250	9.7650	4.8750	9.4400	8.7500	9.2850
1.2500	9.7500	5.0000	9.4350	8.8750	9.2800
1.3750	9.7350	5.1250	9.4250	9.0000	9.2800
1.5000	9.7200	5.2500	9.4200	9.1250	9.2750
1.6250	9.7050	5.3750	9.4100	9.2500	9.2750
1.7500	9.6900	5.5000	9.4100	9.3750	9.2700
1.8750	9.6800	5.6250	9.4050	9.5000	9.2700
2.0000	9.6700	5.7500	9.3950	9.6250	9.2650
2.1250	9.6550	5.8750	9.3900	9.7500	9.2650
2.2500	9.6400	6.0000	9.3850	9.8750	9.2600
2.3750	9.6250	6.1250	9.3800	10.0000	9.2550
2.5000	9.6150	6.2500	9.3700	10.1250	9.2500
2.6250	9.6050	6.3750	9.3650	10.2500	9.2450
2.7500	9.5900	6.5000	9.3600	10.3750	9.2450
2.8750	9.5800	6.6250	9.3600	10.5000	9.2450
3.0000	9.5700	6.7500	9.3550	10.6250	9.2400
3.1250	9.5600	6.8750	9.3500	10.7500	9.2400
3.2500	9.5500	7.0000	9.3450	10.8750	9.2350
3.3750	9.5400	7.1250	9.3400	11.0000	9.2300
3.5000	9.5300	7.2500	9.3350	11.1250	9.2300
3.6250	9.5200	7.3750	9.3300		
		7.5000	9.3250		

EXPERIMENT NO. 28

NAHCO3 = 0.1533E-02 NAOH = 0.6690E-03 CACL2 = 0.1323E-02

TEMPERATURE = 0.2110E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	10.0600	8.5000	9.1550
0.2500	10.0100	8.7500	9.1450
0.5000	9.9550	9.0000	9.1350
0.7500	9.9050	9.2500	9.1250
1.0000	9.8550	9.5000	9.1150
1.2500	9.8100	9.7500	9.1050
1.5000	9.7600	10.0000	9.1000
1.7500	9.7200	10.2500	9.0900
2.0000	9.6800	10.5000	9.0850
2.2500	9.6400	10.7500	9.0750
2.5000	9.6050	11.0000	9.0650
2.7500	9.5700	11.2500	9.0600
3.0000	9.5400	11.5000	9.0550
3.2500	9.5100	11.7500	9.0450
3.5000	9.4850	12.0000	9.0400
3.7500	9.4600	12.2500	9.0300
4.0000	9.4300	12.5000	9.0250
4.2500	9.4100	12.7500	9.0200
4.5000	9.3900	13.0000	9.0150
4.7500	9.3700	13.2500	9.0100
5.0000	9.3500	13.5000	9.0050
5.2500	9.3330	13.7500	8.9950
5.5000	9.3100	14.0000	8.9900
5.7500	9.2950	14.2500	8.9850
6.0000	9.2800	14.5000	8.9800
6.2500	9.2650	14.7500	8.9750
6.5000	9.2500	15.0000	8.9700
6.7500	9.2400	15.2500	8.9650
7.0000	9.2250	15.5000	8.9600
7.2500	9.2100	15.7500	8.9550
7.5000	9.2000	16.0000	8.9500
7.7500	9.1900	16.2500	8.9450
8.0000	9.1750		
8.2500	9.1650		

EXPERIMENT NO. 29

NAHCO3 = 0.1533E-02 NAOH = 0.6690E-03 CACL2 = 0.1764E-02

TEMPERATURE = 0.2100E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	10.0200	4.1250	9.0700
0.1250	9.9900	4.2500	9.0500
0.2500	9.9600	4.3750	9.0300
0.3750	9.9100	4.5000	9.0200
0.5000	9.8750	4.6250	9.0050
0.6250	9.8350	4.7500	8.9900
0.7500	9.7950	4.8750	8.9750
0.8750	9.7500	5.0000	8.9650
1.0000	9.7150	5.1250	8.9500
1.1250	9.6800	5.2500	8.9400
1.2500	9.6400	5.3750	8.9300
1.3750	9.6050	5.5000	8.9150
1.5000	9.5700	5.6250	8.9000
1.6250	9.5400	5.7500	8.8900
1.7500	9.5100	5.8750	8.8800
1.8750	9.4750	6.0000	8.8700
2.0000	9.4500	6.2500	8.8500
2.1250	9.4200	6.3750	8.8400
2.2500	9.3900	6.5000	8.8300
2.3750	9.3650	6.6250	8.8200
2.5000	9.3400	6.7500	8.8100
2.6250	9.3150	6.8750	8.8050
2.7500	9.2850	7.0000	8.7950
2.8750	9.2650	7.1250	8.7850
3.0000	9.2450	7.2500	8.7800
3.1250	9.2200	7.3750	8.7700
3.2500	9.2000	7.5000	8.7650
3.3750	9.1800	7.6250	8.7550
3.5000	9.1600	7.7500	8.7500
3.6250	9.1400	7.8750	8.7400
3.7500	9.1200	8.0000	8.7350
3.8750	9.1000	9.1250	8.7300
4.0	9.0900		

EXPERIMENT NO. 30

NAHCO3 = 0.1541E-02 NAOH = 0.6690E-03 CACL2 = 0.1059E-02

TEMPERATURE = 0.2090E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	9.8600	8.2500	9.0600
0.2500	9.8150	8.5000	9.0450
0.5000	9.7650	8.7500	9.0350
0.7500	9.7200	9.0000	9.0250
1.0000	9.6800	9.2500	9.0150
1.2500	9.6350	9.5000	9.0050
1.5000	9.6000	9.7500	8.9950
1.7500	9.5650	10.0000	8.9850
2.0000	9.5350	10.2500	8.9750
2.2500	9.5000	10.5000	8.9700
2.5000	9.4700	10.7500	8.9610
2.7500	9.4450	11.0000	8.9550
3.0000	9.4150	11.2500	8.9450
3.2500	9.3900	11.5000	8.9400
3.5000	9.3600	11.7500	8.9330
3.7500	9.3400	12.0000	8.9250
4.0000	9.3200	12.2500	8.9200
4.2500	9.3000	12.5000	8.9100
4.5000	9.2750	12.7500	8.9050
4.7500	9.2600	13.0000	8.8950
5.0000	9.2450	13.2500	8.8900
5.2500	9.2250	13.5000	8.8850
5.5000	9.2100	13.7500	8.8800
5.7500	9.1900	14.0000	8.8750
6.0000	9.1750	14.2500	8.8650
6.2500	9.1600	14.5000	8.8600
6.5000	9.1500	14.7500	8.8550
6.7500	9.1300	15.0000	8.8500
7.0000	9.1200	15.2500	8.8450
7.2500	9.1050	15.5000	8.8400
7.5000	9.0900	15.7500	8.8350
7.7500	9.0800		
8.0000	9.1700		

EXPERIMENT NO. 31

NAHCO3 = 0.1541E-02 NAOH = 0.6690E-03 CACL2 = 0.1059E-02

TEMPERATURE = 0.2086E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	9.8200	7.2500	8.9800
0.2500	9.7650	7.5000	8.9650
0.5000	9.7300	7.7500	8.9500
0.7500	9.6850	8.0000	8.9350
1.0000	9.6400	8.2500	8.9250
1.2500	9.5980	8.5000	8.9150
1.5000	9.5550	8.7500	8.9050
1.7500	9.5050	9.0000	8.8950
2.0000	9.4700	9.2500	8.8850
2.2500	9.4350	9.5000	8.8750
2.5000	9.4050	9.7500	8.8650
2.7500	9.3700	10.0000	8.8550
3.0000	9.3350	10.2500	8.8500
3.2500	9.3050	10.5000	8.8400
3.5000	9.2800	10.7500	8.8300
3.7500	9.2550	11.0000	8.8200
4.0000	9.2300	11.2500	8.8100
4.2500	9.2050	11.5000	8.8050
4.5000	9.1850	11.7500	8.7950
4.7500	9.1550	12.0000	8.7900
5.0000	9.1350	12.2500	8.7850
5.2500	9.1150	12.5000	8.7800
5.5000	9.0950	12.7500	8.7700
5.7500	9.0750	13.0000	8.7650
6.0000	9.0550	13.2500	8.7650
6.2500	9.0400	13.5000	8.7550
6.5000	9.0250	13.7500	8.7500
6.7500	9.0150		
7.0000	8.9950		

EXPERIMENT NO. 32

NAHCO3 = 0.1541E-02 NAOH = 0.6690E-03 CACL2 = 0.1059E-02

TEMPERATURE = 0.2060E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	9.8200	6.7500	8.9750
0.2500	9.7700	7.0000	8.9650
0.5000	9.7200	7.2500	8.9500
0.7500	9.6700	7.5000	8.9350
1.0000	9.6200	7.7500	8.9250
1.2500	9.5700	8.0000	8.9150
1.5000	9.5250	8.2500	8.9050
1.7500	9.4900	8.5000	8.8950
2.0000	9.4400	8.7500	8.8850
2.2500	9.4100	9.0000	8.8750
2.5000	9.3700	9.2500	8.8650
2.7500	9.3400	9.5000	8.8550
3.0000	9.3150	9.7500	8.8450
3.2500	9.2750	10.0000	8.8350
3.5000	9.2450	10.2500	8.8250
3.7500	9.2150	10.5000	8.8150
4.0000	9.1950	10.7500	8.8110
4.2500	9.1700	11.0000	8.8000
4.5000	9.1450	11.2500	8.7950
4.7500	9.1200	11.5000	8.7850
5.0000	9.1000	11.7500	8.7800
5.2500	9.0800	12.0000	8.7750
5.5000	9.0650	12.2500	8.7650
5.7500	9.0450	12.5000	8.7600
6.0000	9.0250	12.7500	8.7550
6.2500	9.0100	13.0000	8.7500
6.5000	8.9900	13.2500	8.7450

EXPERIMENT NO. 33

NAHCO3 = 0.1541E-02 NAOH = 0.6690E-03 CACL2 = 0.1059E-02

TEMPERATURE = 0.2060E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	9.8300	6.5000	8.9800
0.2500	9.7700	6.7500	8.9600
0.5000	9.7100	7.0000	8.9450
0.7500	9.6550	7.2500	8.9300
1.0000	9.6000	7.5000	8.9150
1.2500	9.5550	7.7500	8.9050
1.5000	9.5000	8.0000	8.8850
1.7500	9.4600	8.2500	8.8700
2.0000	9.4200	8.5000	8.8550
2.2500	9.3850	8.7500	8.8450
2.5000	9.3500	9.0000	8.8300
2.7500	9.3050	9.2500	8.8250
3.0000	9.2750	9.5000	8.8100
3.2500	9.2450	9.7500	8.7950
3.5000	9.2150	10.0000	8.7900
3.7500	9.1850	10.2500	8.7800
4.0000	9.1600	10.5000	8.7700
4.2500	9.1350	10.7500	8.7600
4.5000	9.1100	11.0000	8.7500
4.7500	9.0850	11.2500	8.7450
5.0000	9.0650	11.5000	8.7400
5.2500	9.0450	11.7500	8.7350
5.5000	9.0250	12.0000	8.7300
5.7500	9.0100	12.2500	8.7250

EXPERIMENT NO. 34

NAHCO3 = 0.1533E-02 NAOH = 0.6690E-03 CACL2 = [illegible]

TEMPERATURE = 0.2060E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 500.

TIME	PH	TIME	PH
0.0	9.7900	6.7500	8.9650
0.2500	9.7500	7.0000	8.9500
0.5000	9.7050	7.2500	8.9300
0.7500	9.6550	7.5000	8.9150
1.0000	9.6100	7.7500	8.9000
1.2500	9.5650	8.0000	8.8850
1.5000	9.5200	8.2500	8.8650
1.7500	9.4800	8.5000	8.8700
2.0000	9.4400	8.7500	8.8650
2.2500	9.4050	9.0000	8.8500
2.5000	9.3650	9.2500	8.8400
2.7500	9.3350	9.5000	8.8300
3.0000	9.3000	9.7500	8.8200
3.2500	9.2700	10.0000	8.8100
3.5000	9.2400	10.2500	8.8050
3.7500	9.2150	10.5000	8.8000
4.0000	9.1900	10.7500	8.7950
4.2500	9.1650	11.0000	8.7900
4.5000	9.1400	11.2500	8.7750
4.7500	9.1150	11.5000	8.7650
5.0000	9.0900	11.7500	8.7600
5.2500	9.0750	12.0000	8.7500
5.5000	9.0500	12.2500	8.7450
5.7500	9.0300	12.5000	8.7400
6.0000	9.0100	12.7500	8.7350
6.2500	8.9900	13.0000	8.7300
6.5000	8.9750	13.2500	8.7250
		13.5000	8.7200
		13.7500	8.7150

EXPERIMENT NO. 35

NAHCO3 = [illegible]1533E-02 NAOH = [illegible]6690E-03 CACL2 = 0.1059E-02

TEMPERATURE = [illegible]2060E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = [illegible]

TIME	PH	TIME	PH
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

EXPERIMENT NO. 40

NAHCO3 = 0.3480E-02 NAOH = 0.1310E-02 CACL2 = 0.3730E-02

TEMPERATURE = 0.2460E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.0000

TIME	PH	TIME	PH
0.0	9.6250	1.1670	8.6710
0.0415	9.5850	1.2085	8.6500
0.0830	9.5450	1.2500	8.6200
0.1245	9.5100	1.2915	8.5950
0.1670	9.4700	1.3330	8.5700
0.2085	9.4350	1.3745	8.5420
0.2500	9.3950	1.4160	8.5210
0.2915	9.3550	1.4575	8.5000
0.3330	9.3200	1.5000	8.4700
0.3745	9.2850	1.5415	8.4500
0.4160	9.2500	1.5830	8.4250
0.4575	9.2150	1.6245	8.4100
0.5000	9.1800	1.6670	8.3850
0.5415	9.1450	1.7085	8.3650
0.5830	9.1100	1.7500	8.3450
0.6245	9.0750	1.7915	8.3250
0.6670	9.0400	1.8330	8.3000
0.7085	9.0050	1.8745	8.2900
0.7500	8.9700	1.9170	8.2650
0.7915	8.9350	1.9585	8.2500
0.8330	8.9100	2.0000	8.2350
0.8745	8.8750	2.0415	8.2150
0.9170	8.8450	2.0830	8.2000
0.9585	8.8150	2.1245	8.1850
1.0000	8.7900	2.1670	8.1700
1.0415	8.7600	2.2085	8.1600
1.0830	8.7300	2.2500	8.1450
1.1245	8.7000	2.2915	8.1350

EXPERIMENT NO. 41

NAHCO3 = 0.3478E-02 NAOH = 0.1210E-02 CACL2 = 0.3720E-02

TEMPERATURE = 0.2520E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.5250	1.0415	8.6250
0.0415	9.4750	1.0830	8.5950
0.0830	9.4300	1.1245	8.5650
0.1245	9.3850	1.1670	8.5400
0.1670	9.3400	1.2085	8.5100
0.2085	9.3050	1.2500	8.4850
0.2500	9.2650	1.2915	8.4600
0.2915	9.2250	1.3330	8.4350
0.3330	9.1900	1.3745	8.4100
0.3745	9.1550	1.4160	8.3900
0.4160	9.1150	1.4575	8.3600
0.4575	9.0750	1.5000	8.3400
0.5000	9.0400	1.5415	8.3150
0.5415	9.0000	1.5830	8.2950
0.5830	8.9750	1.6245	8.2750
0.6245	8.9350	1.6670	8.2550
0.6670	8.9050	1.7085	8.2350
0.7085	8.8700	1.7500	8.2150
0.7500	8.8350	1.7915	8.1950
0.7915	8.8050	1.8330	8.1750
0.8330	8.7750	1.8745	8.1600
0.8745	8.7450	1.9170	8.1450
0.9170	8.7150	1.9585	8.1250
0.9585	8.6850	2.0000	8.1150
1.0000	8.6550		

EXPERIMENT NO. 43

NAHCO3 = 0.2305E-02 NAOH = 0.9060E-03 CACL2 = 0.3720E-02

TEMPERATURE = 0.2520E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.5300	1.1245	8.6000
0.0415	9.4850	1.1670	8.5750
0.0830	9.4450	1.2085	8.5450
0.1245	9.4050	1.2500	8.5250
0.1670	9.3600	1.2915	8.5950
0.2085	9.3250	1.3330	8.4700
0.2500	9.2850	1.3745	8.4450
0.2915	9.2450	1.4160	8.4200
0.3330	9.2100	1.4575	8.3950
0.3745	9.1750	1.5000	8.3700
0.4160	9.1400	1.5415	8.3500
0.4575	9.1000	1.5830	8.3300
0.5000	9.0650	1.6245	8.3100
0.5415	9.0300	1.6670	8.2900
0.5830	9.0000	1.7085	8.2700
0.6245	8.9600	1.7500	8.2500
0.7085	8.9000	1.7915	8.2300
0.7500	8.8700	1.8330	8.2150
0.7915	8.8350	1.8745	8.1950
0.8330	8.8050	1.9170	8.1800
0.8745	8.7750	1.9585	8.1650
0.9170	8.7450	2.0000	8.1450
0.9585	8.7150	2.0415	8.1300
1.0000	8.6850	2.0830	8.1200
1.0415	8.6600		
1.0830	8.6300		

EXPERIMENT NO. 45

NAHCO3 = 0.1535E-02 NAOH = 0.6050E-03 CACL2 = 0.3720E-02

TEMPERATURE = 0.2510E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.5100	1.1245	8.6250
0.0415	9.4700	1.1670	8.6000
0.0830	9.4300	1.2085	8.5750
0.1245	9.3950	1.2500	8.5500
0.1670	9.3550	1.2915	8.5250
0.2085	9.3200	1.3330	8.5000
0.2500	9.2800	1.3745	8.4800
0.2915	9.2450	1.4160	8.4550
0.3330	9.2050	1.4575	8.4300
0.3745	9.1700	1.5000	8.4150
0.4160	9.1350	1.5415	8.3950
0.4575	9.1000	1.5830	8.3750
0.5000	9.0650	1.6245	8.3550
0.5415	9.0300	1.6670	8.3350
0.5830	9.0000	1.7085	8.3150
0.6245	8.9700	1.7500	8.2950
0.6670	8.9400	1.7915	8.2800
0.7085	8.9050	1.8330	8.2650
0.7500	8.8750	1.8745	8.2450
0.7915	8.8450	1.9170	8.2300
0.8330	8.8200	1.9585	8.2150
0.8745	8.7900	2.0000	8.1950
0.9170	8.7650	2.0415	8.1850
0.9585	8.7350	2.0830	8.1700
1.0000	8.7150	2.1245	8.1550
1.0415	8.6900	2.1670	8.1450
1.0830	8.6650	2.2085	8.1300

EXPERIMENT NO. 46

NAHCO3 = 0.3460E-02 NAOH = 0.1320E-02 CACL2 = 0.2790E-02

TEMPERATURE = 0.2500E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.6400	1.5000	8.6600
0.0415	9.6100	1.5415	8.6350
0.0830	9.5750	1.5830	8.6150
0.1245	9.5450	1.6245	8.5950
0.1670	9.5100	1.6670	8.5750
0.2085	9.4850	1.7085	8.5550
0.2500	9.4550	1.7500	8.5350
0.2915	9.4200	1.7915	8.5150
0.3330	9.3950	1.8330	8.4950
0.3745	9.3600	1.8745	8.4750
0.4160	9.3300	1.9170	8.4550
0.4575	9.3000	1.9585	8.4400
0.5000	9.2750	2.0000	8.4200
0.5415	9.2450	2.0415	8.4050
0.5830	9.2150	2.0830	8.3900
0.6245	9.1850	2.1245	8.3750
0.6670	9.1550	2.1670	8.3500
0.7085	9.1350	2.2085	8.3400
0.7500	9.1100	2.2500	8.3250
0.7915	9.0750	2.2915	8.3100
0.8330	9.0550	2.3330	8.2950
0.8745	9.0250	2.3745	8.2750
0.9170	8.9950	2.4160	8.2650
0.9585	8.9700	2.4575	8.2550
1.0000	8.9450	2.5000	8.2400
1.0415	8.9200	2.2515	8.2250
1.0830	8.8950	2.5830	8.2150
1.1245	8.8700	2.6245	8.2050
1.1670	8.8450	2.6670	8.1900
1.2085	8.8150	2.7085	8.1800
1.2500	8.7950	2.7500	8.1650
1.2915	8.7700	2.7915	8.1550
1.3330	8.7450	2.8330	8.1450
1.3745	8.7250	2.8745	8.1400
1.4160	8.7000	2.9170	8.1350
1.4575	8.6800	2.9585	8.1200

EXPERIMENT NO. 47

NAHCO3 = 0.3478E-02 NAOH = 0.1210E-02 CACL2 = 0.2790E-02

TEMPERATURE = 0.2600E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH	TIME	PH
0.0	9.6600	1.2085	8.8250	2.3745	8.2900
0.0415	9.6200	1.2500	8.8050	2.4160	8.2750
0.0830	9.5900	1.2915	8.7800	2.4575	8.2650
0.1245	9.5600	1.3330	8.7600	2.5000	8.2500
0.1670	9.5300	1.3745	8.7350	2.5415	8.2400
0.2085	9.4950	1.4160	8.7100	2.5830	8.2250
0.2500	9.4700	1.4575	8.6900	2.6245	8.2200
0.2915	9.4350	1.5000	8.6650	2.6670	8.2050
0.3330	9.4050	1.5415	8.6450	2.7085	8.1950
0.3745	9.3750	1.5830	8.6250	2.7500	8.1850
0.4160	9.3450	1.6245	8.6050	2.7915	8.1700
0.4575	9.3150	1.6670	8.5850	2.8330	8.1650
0.5000	9.2850	1.7085	8.5650	2.8745	8.1550
0.5415	9.2550	1.7500	8.5450	2.9170	8.1450
0.5830	9.2200	1.7915	8.5200	2.9585	8.1350
0.6245	9.1950	1.8330	8.5000	3.0000	8.1250
1.6670	9.1650	1.8745	8.4850	3.0415	8.1200
0.7085	9.1400	1.9170	8.4650	3.0830	8.1100
0.7500	9.1150	1.9585	8.4450	3.1245	8.1000
0.7915	9.0850	2.0000	8.4300	3.1670	8.0900
0.8330	9.0550	2.0415	8.4150	3.2085	8.0850
0.8745	9.0300	2.0830	8.3950	3.2500	8.0800
0.9170	9.0050	2.1245	8.3800	3.2915	8.0700
0.9585	8.9800	2.1670	8.3650	3.3330	8.0650
1.0000	8.9550	2.2085	8.3550	3.3745	8.0600
1.0415	8.9250	2.2500	8.3350	3.4160	8.0500
1.0830	8.9000	2.2915	8.3200	3.4575	8.0450
1.1245	8.8750	2.3330	8.3100		
1.1670	8.8500				

EXPERIMENT NO. 48

NAHCO3 = 0.2790E-02 NAOH = 0.1060E-02 CACL2 = 0.2790E-02

TEMPERATURE = 0.2480E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.0

TIME	PH	TIME	PH
0.0	9.6600	1.1670	8.8000
0.0415	9.6300	1.2085	8.7750
0.0830	9.5950	1.2500	8.7550
0.1245	9.5600	1.2915	8.7250
0.1670	9.5200	1.3330	8.7000
0.2085	9.4900	1.3745	8.6800
0.2500	9.4550	1.4160	8.6550
0.2915	9.4200	1.4575	8.6350
0.3330	9.3850	1.5000	8.6100
0.3745	9.3550	1.5415	8.5900
0.4160	9.3200	1.5830	8.5650
0.4575	9.2900	1.6245	8.5450
0.5000	9.2600	1.6670	8.5250
0.5415	9.2250	1.7085	8.5050
0.5830	9.1950	1.7500	8.4800
0.6245	9.1600	1.7915	8.4650
0.6670	9.1350	1.8330	8.4450
0.7085	9.1000	1.8745	8.4300
0.7500	9.0700	1.9170	8.4150
0.7915	9.0450	1.9585	8.3950
0.8330	9.0150	2.0000	8.3800
0.8745	8.9850	2.0415	8.3650
0.9170	8.9550	2.0830	8.3500
0.9585	8.9350	2.1245	8.3350
1.0000	8.9150	2.1670	8.3200
1.0415	8.8850	2.2085	8.3050
1.0830	8.8550	2.2500	8.2900
1.1245	8.8250	2.2915	8.2750

EXPERIMENT NO. 49

NAHCO3 = 0.2305E-02 NAOH = 0.9060E-03 CACL2 = 0.2790E-02

TEMPERATURE = 0.2600E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.0

TIME	PH	TIME	PH	TIME	PH
0.0	9.6550	1.2915	8.7550	2.5415	8.2350
0.0415	9.6150	1.3330	8.7350	2.5830	8.2200
0.0830	9.5800	1.3745	8.7100	2.6245	8.2100
0.1245	9.5550	1.4160	8.6900	2.6670	8.2050
0.1670	9.5100	1.4575	8.6650	2.7085	8.1900
0.2085	9.4750	1.5000	8.6450	2.7500	8.1800
0.2500	9.4500	1.5415	8.6250	2.7915	8.1700
0.2915	9.4150	1.5830	8.6050	2.8330	8.1600
0.3330	9.3800	1.6245	8.5850	2.8745	8.1500
0.3745	9.3550	1.6670	8.5650	2.9170	8.1450
0.4160	9.3200	1.7085	8.5500	2.9585	8.1350
0.4575	9.2900	1.7500	8.5300	3.0000	8.1300
0.5000	9.2600	1.7915	8.5100	3.0415	8.1150
0.5415	9.2300	1.8330	8.4900	3.0830	8.1100
0.5830	9.2000	1.8745	8.4750	3.1245	8.1000
0.6245	9.1700	1.9170	8.4550	3.1670	8.0900
0.6670	9.1450	1.9585	8.4400	3.2085	8.0850
0.7085	9.1150	2.0000	8.4200	3.2500	8.0750
0.7500	9.0850	2.0415	8.4050	3.2915	8.0700
0.7915	9.0550	2.0830	8.3850	3.3330	8.0650
0.8330	9.0350	2.1245	8.3700	3.3745	8.0550
0.8745	9.0050	2.1670	8.3550	3.4160	8.0500
0.9170	8.9900	2.2085	8.3450	3.4575	8.0450
0.9585	8.9550	2.2500	8.3300	3.5000	8.0400
1.0000	8.9250	2.2915	8.3150	3.5415	8.0350
1.0415	8.9000	2.3330	8.3000	3.5830	8.0250
1.0830	8.8750	2.3745	8.2850	3.6245	8.0200
1.1245	8.8500	2.4160	8.2700	3.6670	8.0150
1.1670	8.8250	2.4575	8.2600	3.7085	8.0100
1.2085	8.8000	2.5000	8.2500		
1.2500	8.7750				

EXPERIMENT NO. 50

NAHCO3 = 0.1920E-02 NAOH = 0.7560E-03 CACL2 = 0.2790E-02

TEMPERATURE = 0.2460E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH	TIME	PH
0.0	9.6300	1.2915	8.7550	2.5415	8.2550
0.0415	9.5900	1.3330	8.7250	2.5830	8.2450
0.0830	9.5600	1.3745	8.7100	2.6245	8.2350
0.1245	9.5300	1.4160	8.6850	2.6670	8.2250
0.1670	9.4950	1.4575	8.6650	2.7085	8.2150
0.2085	9.4600	1.5000	8.6450	2.7500	8.2050
0.2500	9.4300	1.5415	8.6250	2.7915	8.1950
0.2915	9.4000	1.5830	8.6050	2.8330	8.1850
0.3330	9.3700	1.6245	8.5850	2.8745	8.1750
0.3745	9.3350	1.6670	8.5650	2.9170	8.1650
0.4160	9.3050	1.7085	8.5500	2.9585	8.1550
0.4575	9.2700	1.7500	8.5300	3.0000	8.1450
0.5000	9.2400	1.7915	8.5150	3.0415	8.1350
0.5415	9.2150	1.8330	8.4950	3.0830	8.1250
0.5830	9.1850	1.8745	8.4800	3.1245	8.1250
0.6245	9.1550	1.9170	8.4600	3.1670	8.1150
0.6670	9.1250	1.9585	8.4500	3.2085	8.1050
0.7085	9.1000	2.0000	8.4300	3.2500	8.1050
0.7500	9.0750	2.0415	8.4100	3.2915	8.0950
0.7915	9.0500	2.0830	8.4000	3.3330	8.0850
0.8330	9.0250	2.1245	8.3800	3.3745	8.0850
0.8745	8.9950	2.1670	8.3650	3.4160	8.0750
0.9170	8.9650	2.2085	8.3550	3.4575	8.0750
0.9585	8.9450	2.2500	8.3400	3.5000	8.0650
1.0000	8.9150	2.2915	8.3300	3.5415	8.0650
1.0415	8.8950	2.3330	8.3150	3.5830	8.0550
1.0830	8.8700	2.3745	8.3050	3.6245	8.0450
1.1245	8.8450	2.4160	8.2850	3.6670	8.0450
1.1670	8.8250	2.4160	8.2950	3.7085	8.0350
1.2085	8.8050	2.4575	8.2750		
1.2500	8.7750	2.5000	8.2650		

EXPERIMENT NO. 52

NAHCO3 = 0.2460E-02 NAOH = 0.1320E-02 CACL2 = 0.1860E-02

TEMPERATURE = 0.2440E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.8100	2.0830	8.7650
0.0830	9.7550	2.9170	8.7400
0.1670	9.7200	3.0000	8.7250
0.2500	9.6700	3.0830	8.7050
0.3330	9.6300	3.1670	8.6900
0.4160	9.5900	3.2500	8.6750
0.5000	9.5450	3.3330	8.6600
0.5830	9.5000	3.4160	8.6450
0.6670	9.4650	3.5000	8.6300
0.7500	9.4300	3.5830	8.6200
0.8330	9.3900	3.6670	8.6050
0.9170	9.3500	3.7500	8.5900
1.0000	9.3200	3.8330	8.5850
1.0830	9.2900	3.9170	8.5700
1.1670	9.2500	4.0000	8.5550
1.2500	9.2200	4.0830	8.5450
1.3330	9.1900	4.1670	8.5350
1.4160	9.1600	4.2500	8.5250
1.5000	9.1300	4.3330	8.5150
1.5830	9.1000	4.4160	8.5100
1.6670	9.0700	4.5000	8.5000
1.7500	9.0400	4.5830	8.4850
1.8330	9.0100	4.6670	8.4750
1.9170	8.9850	4.7500	8.4700
2.0000	8.9700	4.8330	8.4650
2.0830	8.9450	4.9170	8.4550
2.1670	8.9200	5.0000	8.4500
2.2500	8.9000	5.0830	8.4450
2.3330	8.8750	5.1670	8.4350
2.4160	8.8550	5.2500	8.4300
2.5000	8.8350	5.3330	8.4250
2.5830	8.8150	5.4160	8.4150
2.6670	8.7950		
2.7500	8.7750		

EXPERIMENT NO. 53

NAHCO3 = 0.3070E-02 NAOH = 0.1210E-02 CACL2 = 0.1860E-02

TEMPERATURE = 0.2450E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.7500	2.7500	8.6200
0.0830	9.7000	2.8330	8.6600
0.1670	9.5500	2.9170	8.5800
0.2500	9.6000	3.0000	8.5600
0.3330	9.5600	3.0830	8.5400
0.4160	9.5100	3.1670	8.5250
0.5000	9.4600	3.2500	8.5100
0.5830	9.4200	3.3330	8.4900
0.6670	9.3700	3.4160	8.4800
0.7500	9.3300	3.5000	8.4650
0.8330	9.2900	3.5830	8.4550
0.9170	9.2500	3.6670	8.4450
1.0000	9.2100	3.7500	8.4300
1.0830	9.1700	3.8330	8.4150
1.1670	9.1350	3.9170	8.4050
1.2500	9.1000	4.0000	8.3950
1.3330	9.0700	4.0830	8.3850
1.4160	9.0300	4.1670	8.3750
1.5000	9.0000	4.2500	8.3650
1.5830	8.9700	4.3330	8.3550
1.6670	8.9400	4.4160	8.3450
1.7500	8.9100	4.5000	8.3350
1.8330	8.8800	4.5830	8.3250
1.9170	8.8500	4.6670	8.3150
2.0000	8.8250	4.7500	8.3100
2.0830	8.8000	4.8330	8.3050
2.1670	8.7700	4.9170	8.2950
2.2500	8.7450	5.0000	8.2900
2.3330	8.7250	5.0830	8.2850
2.4160	8.7000	5.1670	8.2800
2.5000	8.6800	5.2500	8.2700
2.5830	8.6600	5.3330	8.2650
2.1670	8.6400	5.4160	8.2600

EXPERIMENT NO. 54

NAHCO3 = 0.2680E-02 NAOH = 0.1060E-02 CACL2 = 0.1940E-02

TEMPERATURE = 0.2500E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.7600	2.7500	8.5350
0.0830	9.7100	2.8330	8.5150
0.1670	9.6550	2.9170	8.4950
0.2500	9.6050	3.0000	8.4750
0.3330	9.5550	3.0830	8.4600
0.4160	9.5100	3.1670	8.4400
0.5000	9.4500	3.2500	8.4200
0.5830	9.4100	3.3330	8.4000
0.6670	9.3650	3.4160	8.3850
0.7500	9.3150	3.5000	8.3700
0.8330	9.2700	3.5830	8.3600
0.9170	9.2250	3.6670	8.3400
1.0000	9.1850	3.7500	8.3250
1.0830	9.1450	3.8330	8.3150
1.1670	9.1050	3.9170	8.3050
1.2500	9.0700	4.0000	8.2950
1.3330	9.0330	4.0830	8.2850
1.4160	8.9950	4.1670	8.2750
1.5000	8.9600	4.2500	8.2650
1.5830	8.9250	4.3330	8.2550
1.6670	8.8900	4.4160	8.2450
1.7500	8.8550	4.5000	8.2350
1.8330	8.8250	4.5830	8.2300
1.9170	8.7900	4.6670	8.2200
2.0000	8.7650	4.7500	8.2100
2.0830	8.7350	4.8330	8.2050
2.1670	8.7100	4.9170	8.2000
2.2500	8.6850	5.0000	8.1950
2.3330	8.6550	5.0830	8.1900
2.4160	8.6300	5.1670	8.1850
2.5000	8.6100	5.2500	8.1750
2.5830	8.5900	5.3330	8.1700
2.1667	8.5700	5.4160	8.1650

EXPERIMENT NO. 55

NAHCO3 = 0.2300E-02 NAOH = 0.9060E-03 CACL2 = 0.1940E-02

TEMPERATURE = 0.2510E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.7400	2.7500	8.4700
0.0830	9.6800	2.8330	8.4450
0.1670	9.6250	2.9170	8.4250
0.2500	9.5700	3.0000	8.4100
0.3330	9.5200	3.0830	8.3900
0.4160	9.4650	3.1670	8.3700
0.5000	9.4100	3.2500	8.3550
0.5830	9.3600	3.3330	8.3400
0.6670	9.3150	3.4160	8.3250
0.7500	9.2700	3.5000	8.3100
0.8330	9.2200	3.5830	8.3000
0.9170	9.1700	3.6670	8.2900
1.0000	9.1300	3.7500	8.2750
1.0830	9.0850	3.8330	8.2650
1.1670	9.0500	3.9170	8.2550
1.2500	9.0050	4.0000	8.2450
1.3330	8.9650	4.0830	8.2350
1.4160	8.9250	4.1670	8.2250
1.5000	8.8900	4.2500	8.2150
1.5830	8.8550	4.3330	8.2050
1.6670	8.8200	4.4160	8.2000
1.7500	8.7850	4.5000	8.1950
1.8330	8.7550	4.5830	8.1850
1.9170	8.7250	4.6670	8.1800
2.0000	8.6950	4.7500	8.1700
2.0830	8.6650	4.8330	8.1650
2.1670	8.6400	4.9170	8.1600
2.2500	8.6100	5.0000	8.1550
2.3330	8.5800	5.0830	8.1500
2.4160	8.5600	5.1670	8.1450
2.5000	8.5350	5.2500	8.1400
2.5830	8.5100	5.3330	8.1350
2.6670	8.4900	5.4160	8.1300

EXPERIMENT NO. 56

NAHCO3 = 0.1915E-02 NAOH = 0.7560E-03 CACL2 = 0.1940E-02

TEMPERATURE = 0.2470E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH
0.0	9.7000	2.7500	8.4500
0.0830	9.6600	2.8330	8.4300
0.1670	9.6100	2.9170	8.4150
0.2500	9.5550	3.0000	8.3850
0.3330	9.5100	3.0830	8.3700
0.4160	9.4450	3.1670	8.3500
0.5000	9.3950	3.2500	8.3350
0.5830	9.3400	3.3330	8.3200
0.6670	9.2950	3.4160	8.3050
0.7500	9.2500	3.5000	8.2900
0.8330	9.2000	3.5830	8.2800
0.9170	9.1550	3.6670	8.2650
1.0000	9.1100	3.7500	8.2550
1.0830	9.0700	3.8330	8.2450
1.1670	9.0300	3.9170	8.2350
1.2500	8.9900	4.0000	8.2200
1.3330	8.9500	4.0830	8.2100
1.4160	8.9150	4.1670	8.1950
1.5000	8.8700	4.2500	8.1850
1.5830	8.8400	4.3330	8.1800
1.6670	8.8000	4.4160	8.1700
1.7500	8.7700	4.5000	8.1650
1.8330	8.7450	4.5830	8.1550
1.9170	8.7150	4.6670	8.1500
2.0000	8.6800	4.7500	8.1450
2.0830	8.6450	4.8330	8.1350
2.1670	8.6200	4.9170	8.1300
2.2500	8.5950	5.0000	8.1250
2.3330	8.5650	5.0830	8.1200
2.4160	8.5400	5.1670	8.1150
2.5000	8.5150	5.2500	8.1100
2.5830	8.4950	5.3330	8.1050
2.6670	8.4700	5.4160	8.1000

EXPERIMENT NO. 34 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2467E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 1000.

TIME	PH	TIME	PH	TIME	PH
0.2080	9.7500	1.4580	9.3200	2.6670	9.0750
0.2500	9.7330	1.5000	9.3100	2.7080	9.0700
0.2920	9.7100	1.5420	9.3000	2.7500	9.0650
0.3330	9.6900	1.5830	9.2900	2.7920	9.0600
0.3750	9.6700	1.6250	9.2800	2.8330	9.0550
0.4170	9.6500	1.6670	9.2700	2.8750	9.0460
0.4580	9.6300	1.7080	9.2550	2.9170	9.0400
0.5000	9.6100	1.7500	9.2450	2.9580	9.0350
0.5420	9.5900	1.7920	9.2400	3.0000	9.0300
0.5830	9.5750	1.8330	9.2300	3.0830	9.0200
0.6250	9.5600	1.8750	9.2200	3.1670	9.0100
0.6670	9.5450	1.9170	9.2100	3.2500	9.0000
0.7080	9.5300	1.9580	9.2050	3.3330	8.9900
0.7500	9.5200	2.0000	9.1950	3.4160	8.9800
0.7920	9.5050	2.0420	9.1950	3.5000	8.9700
0.8330	9.4950	2.0830	9.1800	3.5830	8.9600
0.8750	9.4800	2.1250	9.1700	3.6670	8.9500
0.9170	9.4650	2.1670	9.1650	3.7500	8.9400
0.9580	9.4550	2.2080	9.1550	3.8330	8.9300
1.0000	9.4450	2.2500	9.1500	3.9170	8.9250
1.0420	9.4250	2.2920	9.1400	4.0000	8.9150
1.0830	9.4150	2.3330	9.1350	4.0830	8.9100
1.1250	9.4000	2.3750	9.1250	4.1670	8.9000
1.1670	9.3900	2.4160	9.1200	4.2500	8.8950
1.2080	9.3800	2.4580	9.1100	4.3330	8.8850
1.2500	9.3700	2.5000	9.1050	4.4160	8.8750
1.2920	9.3600	2.5420	9.0950	4.5000	8.8700
1.3330	9.3500	2.5830	9.0900		
1.3750	9.3400	2.6250	9.0850		
1.4160	9.3300				

EXPERIMENT NO. 35 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2472E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 900.

TIME	PH	TIME	PH	TIME	PH
0.2920	9.7100	1.5420	9.3100	2.7920	9.0850
0.3330	9.6950	1.5830	9.3000	2.8330	9.0500
0.3750	9.6800	1.6250	9.2900	2.8750	9.0450
0.4160	9.6600	1.6670	9.2800	2.9170	9.0400
0.4580	9.6450	1.7080	9.2700	2.9580	9.0350
0.5000	9.6300	1.7500	9.2600	3.0000	9.0250
0.5420	9.6100	1.7920	9.2500	3.0830	9.0150
0.5830	9.5950	1.8330	9.2400	3.1670	9.0000
0.6250	9.5800	1.8750	9.2300	3.2500	8.9900
0.6670	9.5600	1.9170	9.2200	3.3330	8.9750
0.7080	9.5450	1.9580	9.2100	3.4160	8.9650
0.7500	9.5350	2.0000	9.2050	3.5000	8.9600
0.7920	9.5200	2.0420	9.1900	3.5830	8.9550
0.8330	9.5150	2.0830	9.1800	3.6670	8.9450
0.8750	9.4950	2.1250	9.1750	3.7500	8.9300
0.9170	9.4800	2.1670	9.1650	3.8330	8.9250
0.9580	9.4650	2.2080	9.1600	3.9170	8.9050
1.0000	9.4550	2.2500	9.1500	4.0000	8.9000
1.0420	9.4450	2.2920	9.1400	4.0830	8.8900
1.0830	9.4300	2.3330	9.1350	4.1670	8.8800
1.1250	9.4200	2.3750	9.1250	4.2500	8.8700
1.1670	9.4100	2.4160	9.1200	4.3330	8.8650
1.2080	9.3950	2.4580	9.1100	4.4160	8.8600
1.2500	9.3850	2.5000	9.1050	4.5000	8.8500
1.2920	9.3750	2.5420	9.0900	4.5830	8.8450
1.3330	9.3650	2.5830	9.0850	4.6670	8.8400
1.3750	9.3600	2.6250	9.0800	4.7500	8.8300
1.4160	9.3450	2.6670	9.0750	4.8330	8.8250
1.4580	9.3300	2.7080	9.0700	4.9170	8.8150
1.5000	9.3200	2.7500	9.0650		

EXPERIMENT NO. 36 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2500E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 800.

TIME	PH	TIME	PH	TIME	PH
0.5420	9.6300	2.9580	9.1000	1.7500	9.3150
0.5830	9.6200	3.0000	9.0900	1.7920	9.3050
0.6250	9.6050	3.0830	9.0800	1.8330	9.2950
0.6670	9.5900	3.1670	9.0650	1.8750	9.2800
0.7080	9.5800	3.2500	9.0550	1.9170	9.2600
0.7500	9.5650	3.3330	9.0450	1.9580	9.2700
0.7920	9.5550	3.4160	9.0300	2.0000	9.2600
0.8330	9.5400	3.5000	9.0200	2.0420	9.2550
0.8750	9.5300	3.5830	9.0100	2.0830	9.2450
0.9170	9.5150	3.6670	9.0000	2.1250	9.2400
0.9580	9.5050	3.7500	8.9900	2.1670	9.2300
1.0000	9.4950	3.8330	8.9800	2.2080	9.2250
1.0420	9.4850	3.9170	8.9700	2.2500	9.2150
1.0830	9.4750	4.0000	8.9600	2.2920	9.2100
1.1250	9.4600	4.0830	8.9500	2.3330	9.2050
1.1670	9.4500	4.1670	8.9400	2.3750	9.1950
1.2080	9.4400	4.2500	8.9300	2.4160	9.1850
1.2500	9.4300	4.3330	8.9250	2.4580	9.1800
1.2920	9.4200	4.4160	8.9150	2.5000	9.1700
1.3330	9.4100	4.5000	8.9050	2.5420	9.1650
1.3750	9.4000	4.5830	8.9000	2.5830	9.1550
1.4160	9.3900	4.6670	8.8950	2.6250	9.1500
1.4580	9.3850	4.7500	8.8900	2.6670	9.1450
1.5000	9.3750	4.8330	8.8800	2.7080	9.1350
1.5420	9.3650	4.9170	8.8750	2.7500	9.1300
1.5830	9.3500	5.0000	8.8700	2.7920	9.1250
1.6250	9.3400	5.0830	8.8600	2.8330	9.12
1.6670	9.3300	5.1670	8.8550	2.87	9.
1.7080	9.3200	5.2500	8.8450	2.91	9.
		5.3330	8.8400		

EXPERIMENT NO. 37 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2500E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 700.

TIME	PH	TIME	PH	TIME	PH
0.2500	9.6800	1.5000	9.3200	2.7500	9.0550
0.2920	9.6650	1.5420	9.3150	2.7920	9.0400
0.3330	9.6550	1.5830	9.3050	2.8330	9.0300
0.3750	9.6350	1.6250	9.2950	2.8750	9.0250
0.4160	9.6200	1.6670	9.2850	2.9170	9.0100
0.4580	9.6050	1.7080	9.2800	2.9580	9.0050
0.5000	9.5900	1.7500	9.2700	3.0000	9.0000
0.5420	9.5800	1.7920	9.2550	3.0830	8.9850
0.5830	9.5650	1.8330	9.2400	3.1670	8.9750
0.6250	9.5500	1.8750	9.2350	3.2500	8.9650
0.6670	9.5400	1.9170	9.2250	3.3330	8.9500
0.7080	9.5250	1.9580	9.2150	3.4160	8.9450
0.7500	9.5150	2.0000	9.2050	3.5000	8.9350
0.7920	9.4950	2.0420	9.2000	3.5830	8.9250
0.8330	9.4850	2.0830	9.1900	3.6670	8.9100
0.8750	9.4700	2.1250	9.1800	3.7500	8.9050
0.9170	9.4600	2.1670	9.1700	3.8330	8.8950
0.9580	9.4500	2.2080	9.1650	3.9170	8.8850
1.0000	9.4400	2.2500	9.1550	4.0000	8.8750
1.0420	9.4300	2.2920	9.1500	4.0830	8.8650
1.0830	9.4200	2.3330	9.1400	4.1670	8.8550
1.1250	9.4050	2.3750	9.1350	4.2500	8.8450
1.1670	9.3950	2.4160	9.1250	4.3330	8.8400
1.2080	9.3850	2.4580	9.1200	4.4160	8.8300
1.2500	9.3800	2.5000	9.1100	4.5000	8.8250
1.2920	9.3700	2.5420	9.1050	4.5830	8.8150
1.3330	9.3600	2.5830	9.0950	4.6670	8.8050
1.3750	9.3500	2.6250	9.0900	4.7500	8.8000
1.4160	9.3400	2.6670	9.0800	4.8330	8.7900
1.4580	9.3300	2.7080	9.0750	4.9170	8.7850
				5.0000	8.7750
				5.0830	8.7650
				5.1670	8.7600
				5.2500	8.7500
				5.3330	8.7400

EXPERIMENT NO. 38 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2450E+02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = [illegible]

TIME	PH	TIME	PH	TIME	PH
0.2080	9.7550	1.5830	9.4250	4.2330	9.0550
0.2500	9.7410	1.6670	9.4100	4.4160	9.0500
0.2920	9.7250	1.7500	9.3950	4.5000	9.0400
0.3330	9.7150	1.8330	9.3800	4.5830	9.0350
0.3750	9.7000	1.9170	9.3600	4.6670	9.0250
0.4160	9.6900	2.0000	9.3500	4.7500	9.0150
0.4580	9.6750	2.0830	9.3300	4.8330	9.0100
0.5000	9.6650	2.1670	9.3200	4.9170	9.0000
0.5420	9.6550	2.2500	9.3050	5.0000	8.9900
0.5830	9.6400	2.3330	9.2950	5.0830	8.9800
0.6250	9.6300	2.4160	9.2800	5.1670	8.9750
0.6670	9.6150	2.5000	9.2650	5.2500	8.9600
0.7080	9.6050	2.5830	9.2550	5.3330	8.9500
0.7500	9.5950	2.6670	9.2450	5.4160	8.9450
0.7920	9.5850	2.7500	9.2350	5.5000	8.9350
0.8330	9.5750	2.8330	9.2200	5.5830	8.9250
0.8750	9.5600	2.9170	9.2100	5.6670	8.9150
0.9170	9.5500	3.0000	9.2000	5.7500	8.9050
0.9580	9.5450	3.0830	9.1900	5.8330	8.8950
1.0000	9.5350	3.1670	9.1800	6.0000	8.9250
1.0420	9.5250	3.2500	9.1650	6.1670	8.9150
1.0830	9.5200	3.3330	9.1550	6.2330	8.9050
1.1250	9.5100	3.4160	9.1450	6.5000	8.9950
1.1670	9.5050	3.5000	9.1350	6.6670	8.8850
1.2080	9.4950	3.5830	9.1250	6.8330	8.8750
1.2500	9.4900	3.6670	9.1200	7.0000	8.8700
1.2920	9.4850	3.7500	9.1100	7.1670	8.8650
1.3330	9.4750	3.8330	9.1000	7.3330	8.8500
1.3750	9.4650	3.9170	9.0950	7.5000	8.8400
1.4160	9.4600	4.0000	9.0900	7.6670	8.8300
1.4580	9.4550	4.0830	9.0800	7.8330	8.8250
1.5000	9.4450	4.1670	9.0700		
		4.2500	9.0650		

EXPERIMENT NO. 39 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2540E+02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = [illegible]

TIME	PH	TIME	PH	TIME	PH
0.2080	9.7750	1.2330	9.6200	3.2330	9.2250
0.2500	9.7650	1.2750	9.5150	3.4160	9.2100
0.2920	9.7500	1.4160	9.5050	3.5000	9.2000
0.3330	9.7400	1.4580	9.4900	3.5830	9.1900
0.3750	9.7300	1.5000	9.4750	3.6670	9.1850
0.4160	9.7150	1.5830	9.4600	3.7500	9.1750
0.4580	9.7050	1.6670	9.4500	3.8330	9.1650
0.5000	9.6950	1.7500	9.4450	3.9170	9.1600
0.5420	9.6900	1.8330	9.4350	4.0000	9.1500
0.5830	9.6800	1.9170	9.4200	4.1670	9.1350
0.6250	9.6700	2.0000	9.4050	4.2500	9.1150
0.6670	9.6550	2.0830	9.3900	4.4160	9.1050
0.7080	9.6500	2.1670	9.3800	4.6670	9.0900
0.7500	9.6400	2.2500	9.3650	4.8330	9.0750
0.7920	9.6300	2.3330	9.3550	5.0000	9.0650
0.8330	9.6200	2.4160	9.3450	5.1670	9.0550
0.8750	9.6100	2.5000	9.3350	5.3330	9.0450
0.9170	9.6000	2.5830	9.3250	5.5000	9.0350
0.9580	9.5900	2.6670	9.3150	5.6670	9.0250
1.0000	9.5800	2.7500	9.3050	5.8330	9.0150
1.0420	9.5700	2.8330	9.2950	6.0000	9.0050
1.0830	9.5600	2.9170	9.2850	6.1670	8.9950
1.1250	9.5500	3.0000	9.2750	6.3330	8.9850
1.1670	9.5400	3.0830	9.2650	6.5000	8.9750
1.2080	9.5300	3.1670	9.2550	6.6670	8.9650
1.2500	9.5200	3.2500	9.2450	6.8330	8.9550
1.2920	9.5100	3.3330	9.2350	7.0000	8.9450
1.3330	9.5000	3.4160	9.2250	7.1670	8.9350
1.3750	9.4900	3.5000	9.2150	7.3330	8.9250
1.4160	9.4800	3.5830	9.2050	7.5000	8.9150
1.4580	9.4700	3.6670	9.1950	7.6670	8.9050
1.5000	9.4600	3.7500	9.1850	7.8330	8.8950
1.5420	9.4500	3.8330	9.1750		

EXPERIMENT NO. 40 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2450E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 400.

TIME	PH	TIME	PH	TIME	PH
0.1670	9.7800	2.4160	9.4000	4.6670	9.1600
0.2500	9.7600	2.5000	9.3900	4.7500	9.1500
0.3330	9.7400	2.5830	9.3800	4.8330	9.1400
0.4160	9.7200	2.6670	9.3700	4.9170	9.1400
0.5000	9.7050	2.7500	9.3600	5.0000	9.1350
0.5830	9.6900	2.8330	9.3500	5.1670	9.1200
0.6670	9.6700	2.9170	9.3350	5.3330	9.1100
0.7500	9.6500	3.0000	9.3250	5.5000	9.1050
0.8330	9.6350	3.0830	9.3200	5.6670	9.0850
0.9170	9.6200	3.1670	9.3100	5.8330	9.0700
1.0000	9.6050	3.2500	9.3000	6.0000	9.0600
1.0830	9.5950	3.3330	9.2950	6.1670	9.0500
1.1670	9.5800	3.4160	9.2850	6.3330	9.0350
1.2500	9.5650	3.5000	9.2750	6.5000	9.0250
1.3330	9.5550	3.5830	9.2700	6.6670	9.0150
1.4160	9.5470	3.6670	9.2600	6.8330	9.0050
1.5000	9.5300	3.7500	9.2500	7.0000	8.9950
1.5830	9.5150	3.8330	9.2400	7.1670	8.9850
1.6670	9.5000	3.9170	9.2300	7.3330	8.9750
1.7500	9.4850	4.0000	9.2250	7.5000	8.9700
1.8330	9.4750	4.0830	9.2150	7.6675	8.9600
1.9170	9.4600	4.1670	9.2050	7.8330	8.9550
2.0000	9.4500	4.2500	9.1950	8.0000	8.9450
2.0830	9.4400	4.3330	9.1850	8.1670	8.9400
2.1670	9.4300	4.4167	9.1800	8.3330	8.9350
2.2500	9.4200	4.5000	9.1700	8.5000	8.9300
2.3330	9.4100	4.5830	9.1650	8.6670	8.9150
				8.8330	8.9100

EXPERIMENT NO. 41 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-02 CACL2 = 0.9648E-03

TEMPERATURE = 0.2500E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 300.

TIME	PH	TIME	PH	TIME	PH
1.5000	9.6150	3.8330	9.3800	8.5000	9.0700
1.5830	9.6050	3.9170	9.3700	8.6670	9.0650
1.6670	9.5950	4.0000	9.3650	8.8330	9.0600
1.7500	9.5850	4.1670	9.3500	9.0000	9.0500
1.8330	9.5750	4.3330	9.3350	9.1670	9.0400
1.9170	9.5650	4.5000	9.3250	9.3330	9.0350
2.0000	9.5550	4.6670	9.3100	9.5000	9.0300
2.0830	9.5500	4.8330	9.3000	9.6670	9.0200
2.1670	9.5400	5.0000	9.2850	9.8330	9.0150
2.2500	9.5300	5.1670	9.2750	10.0000	9.0100
2.3330	9.5200	5.3330	9.2600	10.1670	9.0050
2.4160	9.5100	5.5000	9.2450	10.3330	8.9950
2.5000	9.5000	5.6670	9.2350	10.5000	8.9900
2.5830	9.4900	5.8333	9.2200	10.6670	8.9850
2.6670	9.4850	6.0000	9.2100	10.8330	8.9800
2.7500	9.4750	6.1670	9.2000	11.0000	8.9700
2.8330	9.4700	6.3330	9.1900	11.1670	8.9650
2.9170	9.4600	6.5000	9.1800	11.3330	8.9600
3.0000	9.4500	6.6670	9.1700	11.5000	8.9550
3.0830	9.4400	6.8330	9.1600	11.6670	8.9500
3.1670	9.4350	7.0000	9.1500	11.8330	8.9450
3.2500	9.4250	7.1670	9.1400	12.0000	8.9400
3.3330	9.4200	7.3330	9.1300	12.1670	8.9350
3.4160	9.4100	7.5000	9.1250	12.3330	8.9250
3.5000	9.4050	7.6670	9.1150	12.5000	8.9200
3.5830	9.3950	7.8330	9.1050	12.6670	8.9150
3.6670	9.3900	8.0000	9.1000	12.8330	8.9100
3.7500	9.3850	8.1670	8.9950		
		8.3330	8.9900		

EXPERIMENT NO. 42 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2510E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 200.

TIME	PH	TIME	PH	TIME	PH
0.9170	9.7200	3.6670	9.4850	8.6670	9.1850
1.0000	9.7100	3.8330	9.4700	8.8330	9.1750
1.0830	9.7000	4.0000	9.4600	9.0000	9.1650
1.1670	9.6950	4.1670	9.4500	9.1670	9.1600
1.2500	9.6900	4.3330	9.4350	9.3330	9.1500
1.3330	9.6300	4.5000	9.4250	9.5000	9.1450
1.4160	9.6750	4.6670	9.4100	9.6670	9.1350
1.5000	9.6650	4.8330	9.4000	9.8330	9.1300
1.5830	9.6600	5.0000	9.3900	10.0000	9.1200
1.6670	9.6500	5.1670	9.3800	10.3330	9.1100
1.7500	9.6450	5.3330	9.3700	10.6670	9.0950
1.8330	9.6400	5.5000	9.3600	11.0000	9.0800
1.9170	9.6300	5.6670	9.3500	11.3330	9.0700
2.0000	9.6200	5.8330	9.3400	11.6670	9.0600
2.0830	9.6150	6.0000	9.3300	12.0000	9.0450
2.1670	9.6050	6.1670	9.3200	12.3330	9.0350
2.2500	9.6000	6.3330	9.3100	12.6670	9.0300
2.3330	9.5950	6.5000	9.3000	13.0000	9.0200
2.4170	9.5850	6.6670	9.2900	13.3330	9.0150
2.5000	9.5800	6.8330	9.2800	13.6670	8.9950
2.5830	9.5700	7.0000	9.2700	14.0000	8.9850
2.6670	9.5650	7.1670	9.2600	14.3330	8.9800
2.7500	9.5600	7.3330	9.2500	14.6670	8.9700
2.8330	9.5500	7.5000	9.2400	15.0000	8.9600
2.9170	9.5450	7.6670	9.2300	15.3330	8.9550
3.0000	9.5400	7.8330	9.2200	15.6670	8.9450
3.1670	9.5300	8.0000	9.2150	16.0000	8.9350
3.3330	9.5100	8.1670	9.2100	16.3330	8.9250
3.5000	9.5000	8.3330	9.2000	16.6670	8.9200
		8.5000	9.1900		

EXPERIMENT NO. 43 H

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2510E 02DEGREES CELCIUS

CACO3 SEED CRYSTAL CONCENTRATION = 100.

TIME	PH	TIME	PH
2.5000	9.6750	8.5000	9.3950
2.6670	9.6700	8.6330	9.3700
2.8330	9.6550	9.1670	9.3600
3.0000	9.6450	9.5000	9.3500
3.1670	9.6350	9.8330	9.3350
3.3330	9.6300	10.1670	9.3200
3.5000	9.6200	10.5000	9.3100
3.6670	9.6100	10.8330	9.3000
3.8330	9.6050	11.1670	9.2900
4.0000	9.5950	11.5000	9.2800
4.1670	9.5850	11.8330	9.2700
4.3330	9.5750	12.1670	9.2550
4.5000	9.5700	12.5000	9.2500
4.6670	9.5600	12.8330	9.2350
4.8330	9.5500	13.1670	9.2300
5.0000	9.5450	13.5000	9.2150
5.1670	9.5400	13.8330	9.2050
5.3330	9.5300	14.1670	9.2000
5.5000	9.5200	14.5000	9.1900
5.6670	9.5150	14.8330	9.1800
5.8330	9.5050	15.1670	9.1700
6.0000	9.4950	15.5000	9.1650
6.1670	9.4900	15.8330	9.1550
6.3330	9.4800	16.1670	9.1450
6.5000	9.4750	16.5000	9.1350
6.6670	9.4700	16.8330	9.1300
6.8330	9.4600	17.1670	9.1200
7.0000	9.4550	17.5000	9.1100
7.1670	9.4450	17.8330	9.0950
7.3330	9.4400	18.1670	9.0850
7.5000	9.4300	18.5000	9.0800
7.6670	9.4250	18.8330	9.0700
7.8330	9.4150	19.1670	9.0650
8.0000	9.4050	19.5000	9.0550
8.1670	9.4000	19.8330	9.0450
8.3330	9.3900	20.1670	9.0400
		20.5000	9.0300
		20.8330	9.0200
		21.1670	9.0150
		21.5000	9.0050
		21.8330	8.9950
		22.1670	8.9900
		22.5000	8.9800
		22.8330	8.9750
		23.1670	8.9650
		23.5000	8.9550
		23.8330	8.9500
		24.1670	8.9400
		24.5000	8.9350
		24.8330	8.9250
		25.1670	8.9150
		25.5000	8.9100
		25.8330	8.9000
		26.1670	8.8900
		26.5000	8.8850
		26.8330	8.8750
		27.1670	8.8650
		27.5000	8.8600
		27.8330	8.8500
		28.1670	8.8450
		28.5000	8.8350
		28.8330	8.8250
		29.1670	8.8200
		29.5000	8.8100
		29.8330	8.8050
		30.1670	8.7950
		30.5000	8.7850
		30.8330	8.7800
		31.1670	8.7700
		31.5000	8.7650
		31.8330	8.7550
		32.1670	8.7500
		32.5000	8.7400
		32.8330	8.7350
		33.1670	8.7250
		33.5000	8.7200
		33.8330	8.7100
		34.1670	8.7050
		34.5000	8.6950
		34.8330	8.6900
		35.1670	8.6800
		35.5000	8.6750
		35.8330	8.6650
		36.1670	8.6600
		36.5000	8.6500
		36.8330	8.6450
		37.1670	8.6350
		37.5000	8.6300
		37.8330	8.6200
		38.1670	8.6150
		38.5000	8.6050
		38.8330	8.6000
		39.1670	8.5900
		39.5000	8.5850
		39.8330	8.5750
		40.1670	8.5700
		40.5000	8.5600
		40.8330	8.5550
		41.1670	8.5450
		41.5000	8.5400
		41.8330	8.5300
		42.1670	8.5250
		42.5000	8.5150
		42.8330	8.5100
		43.1670	8.5000
		43.5000	8.4950
		43.8330	8.4850
		44.1670	8.4800
		44.5000	8.4700
		44.8330	8.4650
		45.1670	8.4550
		45.5000	8.4500
		45.8330	8.4400
		46.1670	8.4350
		46.5000	8.4250
		46.8330	8.4200
		47.1670	8.4100
		47.5000	8.4050
		47.8330	8.3950
		48.1670	8.3900
		48.5000	8.3800
		48.8330	8.3750
		49.1670	8.3650
		49.5000	8.3600
		49.8330	8.3500
		50.1670	8.3450
		50.5000	8.3350
		50.8330	8.3300
		51.1670	8.3200
		51.5000	8.3150
		51.8330	8.3050
		52.1670	8.3000
		52.5000	8.2900
		52.8330	8.2850
		53.1670	8.2750
		53.5000	8.2700
		53.8330	8.2600
		54.1670	8.2550
		54.5000	8.2450
		54.8330	8.2400
		55.1670	8.2300
		55.5000	8.2250
		55.8330	8.2150
		56.1670	8.2100
		56.5000	8.2000
		56.8330	8.1950
		57.1670	8.1850
		57.5000	8.1800
		57.8330	8.1700
		58.1670	8.1650
		58.5000	8.1550
		58.8330	8.1500
		59.1670	8.1400
		59.5000	8.1350
		59.8330	8.1250
		60.1670	8.1200
		60.5000	8.1100
		60.8330	8.1050
		61.1670	8.0950
		61.5000	8.0900
		61.8330	8.0800
		62.1670	8.0750
		62.5000	8.0650
		62.8330	8.0600
		63.1670	8.0500
		63.5000	8.0450
		63.8330	8.0350
		64.1670	8.0300
		64.5000	8.0200
		64.8330	8.0150
		65.1670	8.0050
		65.5000	7.9950
		65.8330	7.9900
		66.1670	7.9800
		66.5000	7.9750
		66.8330	7.9650
		67.1670	7.9600
		67.5000	7.9500
		67.8330	7.9450
		68.1670	7.9350
		68.5000	7.9300
		68.8330	7.9200
		69.1670	7.9150
		69.5000	7.9050
		69.8330	7.9000
		70.1670	7.8900
		70.5000	7.8850
		70.8330	7.8750
		71.1670	7.8700
		71.5000	7.8600
		71.8330	7.8550
		72.1670	7.8450
		72.5000	7.8400
		72.8330	7.8300
		73.1670	7.8250
		73.5000	7.8150
		73.8330	7.8100
		74.1670	7.8000
		74.5000	7.7950
		74.8330	7.7850
		75.1670	7.7800
		75.5000	7.7700
		75.8330	7.7650
		76.1670	7.7550
		76.5000	7.7500
		76.8330	7.7400
		77.1670	7.7350
		77.5000	7.7250
		77.8330	7.7200
		78.1670	7.7100
		78.5000	7.7050
		78.8330	7.6950
		79.1670	7.6900
		79.5000	7.6800
		79.8330	7.6750
		80.1670	7.6650
		80.5000	7.6600
		80.8330	7.6500
		81.1670	7.6450
		81.5000	7.6350
		81.8330	7.6300
		82.1670	7.6200
		82.5000	7.6150
		82.8330	7.6050
		83.1670	7.6000
		83.5000	7.5900
		83.8330	7.5850
		84.1670	7.5750
		84.5000	7.5700
		84.8330	7.5600
		85.1670	7.5550
		85.5000	7.5450
		85.8330	7.5400
		86.1670	7.5300
		86.5000	7.5250
		86.8330	7.5150
		87.1670	7.5100
		87.5000	7.5000
		87.8330	7.4950
		88.1670	7.4850
		88.5000	7.4800
		88.8330	7.4700
		89.1670	7.4650
		89.5000	7.4550
		89.8330	7.4500
		90.1670	7.4400
		90.5000	7.4350
		90.8330	7.4250
		91.1670	7.4200
		91.5000	7.4100
		91.8330	7.4050
		92.1670	7.3950
		92.5000	7.3900
		92.8330	7.3800
		93.1670	7.3750
		93.5000	7.3650
		93.8330	7.3600
		94.1670	7.3500
		94.5000	7.3450
		94.8330	7.3350
		95.1670	7.3300
		95.5000	7.3200
		95.8330	7.3150
		96.1670	7.3050
		96.5000	7.3000
		96.8330	7.2900
		97.1670	7.2850
		97.5000	7.2750
		97.8330	7.2700
		98.1670	7.2600
		98.5000	7.2550
		98.8330	7.2450
		99.1670	7.2400
		99.5000	7.2300
		99.8330	7.2250
		100.1670	7.2150
		100.5000	7.2100
		100.8330	7.2000
		101.1670	7.1950
		101.5000	7.1850
		101.8330	7.1800
		102.1670	7.1700
		102.5000	7.1650
		102.8330	7.1550
		103.1670	7.1500
		103.5000	7.1400
		103.8330	7.1350
		104.1670	7.1250
		104.5000	7.1200
		104.8330	7.1100
		105.1670	7.1050
		105.5000	7.0950
		105.8330	7.0900
		106.1670	7.0800
		106.5000	7.0750
		106.8330	7.0650
		107.1670	7.0600
		107.5000	7.0500
		107.8330	7.0450
		108.1670	7.0350
		108.5000	7.0300
		108.8330	7.0200
		109.1670	7.0150
		109.5000	7.0050
		109.8330	6.9950
		110.1670	6.9900
		110.5000	6.9800
		110.8330	6.9750
		111.1670	6.9650
		111.5000	6.9600
		111.8330	6.9500
		112.1670	6.9450
		112.5000	6.9350
		112.8330	6.9300
		113.1670	6.9200
		113.5000	6.9150
		113.8330	6.9050
		114.1670	6.9000
		114.5000	6.8900
		114.8330	6.8850
		115.1670	6.8750
		115.5000	6.8700
		115.8330	6.8600
		116.1670	6.8550
		116.5000	6.8450
		116.8330	6.8400
		117.1670	6.8300
		117.5000	6.8250
		117.8330	6.8150
		118.1670	6.8100
		118.5000	6.8000
		118.8330	6.7950
		119.1670	6.7850
		119.5000	6.7800
		119.8330	6.7700
		120.1670	6.7650
		120.5000	6.7550
		120.8330	6.7500
		121.1670	6.7400
		121.5000	6.7350
		121.8330	6.7250
		122.1670	6.7200
		122.5000	6.7100
		122.8330	6.7050
		123.1670	6.6950
		123.5000	6.6900
		123.8330	6.6800
		124.1670	6.6750
		124.5000	6.6650
		124.8330	6.6600
		125.1670	6.6500
		125.5000	6.6450
		125.8330	6.6350
		126.1670	6.6300
		126.5000	6.6200
		126.8330	6.6150
		127.1670	6.6050
		127.5000	6.6000
		127.8330	6.5900
		128.1670	6.5850
		128.5000	6.5750
		128.8330	6.5700
		129.1670	6.5600
		129.5000	6.5550
		129.8330	6.5450
		130.1670	6.5400
		130.5000	6.5300
		130.8330	6.5250
		131.1670	6.5150
		131.5000	6.5100
		131.8330	6.5000
		132.1670	6.4950
		132.5000	6.4850
		132.8330	6.4800
		133.1670	6.4700
		133.5000	6.4650
		133.8330	6.4550
		134.1670	6.4500
		134.5000	6.4400
		134.8330	6.4350
		135.1670	6.4250
		135.5000	6.4200
		135.8330	6.4100
		136.1670	6.4050
		136.5000	6.3950
		136.8330	6.3900
		137.1670	6.3800
		137.5000	6.3750
		137.8330	6.3650
		138.1670	6.3600
		138.5000	6.3500
		138.8330	6.3450
		139.1670	6.3350
		139.5000	6.3300
		139.8330	6.3200
		140.1670	6.3150
		140.5000	6.3050
		140.8330	6.3000
		141.1670	6.2900
		141.5000	6.2850
		141.8330	6.2750
		142.1670	6.2700
		142.5000	6.2600
		142.8330	6.2550
		143.1670	6.2450
		143.5000	6.2400
		143.8330	6.2300
		144.1670	6.2250
		144.5000	6.2150
		144.8330	6.2100
		145.1670	6.2000
		145.5000	6.1950
		145.8330	6.1850
		146.1670	6.1800
		146.5000	6.1700
		146.8330	6.1650
		147.1670	6.1550
		147.5000	6.1500
		147.8330	6.1400
		148.1670	6.1350
		148.5000	6.1250
		148.8330	6.1200
		149.1670	6.1100
		149.5000	6.1050
		149.8330	6.0950
		150.1670	6.0900
		150.5000	6.0800
		150.8330	6.0750
		151.1670	6.0650
		151.5000	6.0600
		151.8330	6.0500
		152.1670	6.0450
		152.5000	6.0350
		152.8330	6.0300
		153.1670	6.0200
		153.5000	6.0150
		153.8330	6.0050
		154.1670	5.9950
		154.5000	5.9900
		154.8330	5.9800
		155.1670	5.9750
		155.5000	5.9650
		155.8330	5.9600
		156.1670	5.9500
		156.5000	5.9450
		156.8330	5.9350
		157.1670	5.9300
		157.5000	5.9200
		157.8330	5.9150
		158.1670	5.9050
		158.5000	5.9000
		158.8330	5.8900
		159.1670	5.8850
		159.5000	5.8750
		159.8330	5.8700
		160.1670	5.8600
		160.5000	5.8550
		160.8330	5.8450
		161.1670	5.8400
		161.5000	5.8300
		161.8330	5.8250
		162.1670	5.8150
		162.5000	5.8100
		162.8330	5.8000
		163.1670	5.7950
		163.5000	5.7850
		163.8330	5.7800
		164.1670	5.7700
		164.5000	5.7650
		164.8330	5.7550
		165.1670	5.7500
		165.5000	5.7400
		165.8330	5.7350
		166.1670	5.7250
		166.5000	5.7200
		166.8330	5.7100
		167.1670	5.7050
		167.5000	5.6950
		167.8330	5.6900
		168.1670	5.6800
		168.5000	5.6750
		168.8330	5.6650
		169.1670	5.6600
		169.5000	5.6500
		169.8330	5.6450
		170.1670	5.6350
		170.5000	5.6300
		170.8330	5.6200
		171.1670	5.6150
		171.5000	5.6050
		171.8330	5.6000
		172.1670	5.5900
		172.5000	5.5850
		172.8330	5.5750
		173.1670	5.5700
		173.5000	5.5600
		173.8330	5.5550
		174.1670	5.5450
		174.5000	5.5400
		174.8330	5.5300
		175.1670	5.5250
		175.5000	5.5150
		175.8330	5.5100
		176.1670	5.5000
		176.5000	5.4950
		176.8330	5.4850
		177.1670	5.4800
		177.5000	5.4700
		177.8330	5.4650
		178.1670	5.4550
		178.5000	5.4500
		178.8330	5.4400
		179.1670	5.4350
		179.5000	5.4250
		179.8330	5.4200
		180.1670	5.4100
		180.5000	5.4050
		180.8330	5.3950
		181.1670	5.3900
		181.5000	5.3800
		181.8330	5.3750
		182.1670	5.3650
		182.5000	5.3600
		182.8330	5.3500
		183.1670	5.3450
		183.5000	5.3350
		183.8330	5.3300
		184.1670	5.3200
		184.5000	5.3150
		184.8330	5.3050
		185.1670	5.3000
		185.5000	5.2900
		185.8330	5.2850
		186.1670	5.2750
		186.5000	5.2700
		186.8330	5.2600
		187.1670	5.2550
		187.5000	5.2450
		187.8330	5.2400
		188.1670	5.2300
		188.5000	5.2250
		188.8330	5.2150
		189.1670	5.2100
		189.5000	5.2000
		189.8330	5.1950
		190.1670	5.1850
		190.5000	5.1800
		190.8330	5.1700
		191.1670	5.1650
		191.5000	5.1550
		191.8330	5.1500
		192.1670	5.1400
		192.5000	5.1350
		192.8330	5.1250
		193.1670	5.1200
		193.5000	5.1100
		193.8330	5.1050
		194.1670	5.0950
		194.5000	5.0900
		194.8330	5.0800
		195.1670	5.0750
		195.5000	5.0650
		195.8330	5.0600
		196.1670	5.0500
		196.5000	5.0450
		196.8330	5.0350
		197.1670	5.0300
		197.5000	5.0200
		197.8330	5.0150
		198.1670	5.0050
		198.5000	4.9950
		198.8330	4.9900
		199.1670	4.9800
		199.5000	4.9750
		199.8330	4.9650
		200.1670	4.9600
		200.5000	4.9500
		200.8330	4.9450
		201.1670	4.9350
		201.5000	4.9300
		201.8330	4.9200
		202.1670	4.9150
		202.5000	4.9050
		202.8330	4.9000
		203.1670	4.8900
		203.5000	4.8850
		203.8330	4.8750
		204.1670	4.8700
		204.5000	4.8600
		204.8330	4.8550
		205.1670	4.8450
		205.5000	4.8400
		205.8330	4.8300
		206.1670	4.8250
		206.5000	4.8150
		206.8330	4.8100
		207.1670	4.8000
		207.5000	4.7950
		207.8330	4.7850
		208.1670	4.7800
		208.5000	4.7700
		208.8330	4.7650
		209.1670	4.7550
		209.5000	4.7500
		209.8330	4.7400
		210.1670	4.7350
		210.5000	4.7250
		210.8330	4.7200
		211.1670	4.7100
		211.5000	4.7050
		211.8330	4.6950
		212.1670	4.6900
		212.5000	4.6800
		212.8330	4.6750
		213.1670	4.6650
		213.5000	4.6600
		213.8330	4.6500
		214.1670	4.6450
		214.5000	4.6350
		214.8330	4.6300
		215.1670	4.6200
		215.5000	4.6150
		215.8330	4.6050
		216.1670	4.6000
		216.5000	4.5900
		216.8330	4.5850
		217.1670	4.5750
		217.5000	4.5700
		217.8330	4.5600
		218.1670	4.5550
		218.5000	4.5450
		218.8330	4.5400
		219.1670	4.5300
		219.5000	4.5250
		219.8330	4.5150
		220.1670	4.5100
		220.5000	4.5000
		220.8330	4.4950
		221.1670	4.4850
		221.5000	4.4800
		221.8330	4.4700
		222.1670	4.4650
		222.5000	4.4550
		222.8330	4.4500
		223.1670	4.4400
		223.5000	4.4350
		223.8330	4.4250
		224.1670	4.4200
		224.5000	4.4100
		224.8330	4.4050
		225.1670	4.3950
		225.5000	4.3900
		225.8330	4.3800
		226.1670	4.3750
		226.5000	4.3650
		226.8330	4.3600
		227.1670	4.3500
		227.5000	4.3450
		227.8330	4.3350
		228.1670	4.3300
		228.5000	4.3200
		228.8330	4.3150
		229.1670	4.3050
		229.5000	4.3000
		229.8330	4.2900
		230.1670	4.2850
		230.5000	4.2750
		230.8330	4.2700
		231.1670	4.2600
		231.5000	4.2550
		231.8330	4.2450
		232.1670	4.2400
		232.5000	4.2300
		232.8330	4.2250
		233.1670	4.2150
		233.5000	4.2100
		233.8330	4.2000
		234.1670	4.1950
		234.5000	4.1850
		234.8330	4.1800
		235.1670	4.1700
		235.5000	4.1650
		235.8330	4.1550
		236.1670	4.1500
		236.5000	4.1400
		236.8330	4.1350
		237.1670	4.1250
		237.5000	4.1200
		237.8330	4.1100
		238.1670	4.1050
		238.5000	4.0950
		238.8330	4.0900
		239.1670	4.0800
		239.5000	4.0750
		239.8330	4.0650
		240.1670	4.0600
		240.5000	4.0500
		240.8330	4.0450
		241.1670	4.0350
		241.5000	4.0300
		241.8330	4.0200
		242.1670	4.0150
		242.5000	4.0050
		242.8330	3.9950
		243.1670	3.9900
		243.5000	3.9800
		243.8330	3.9750
		244.1670	3.9650
		244.5000	3.9600
		244.8330	3.9500
		245.1670	3.9450
		245.5000	3.9350
		245.8330	3.9300
		246.1670	3.9200
		246.5000	3.9150
		246.8330	3.9050
		247.1670	3.9000
		247.5000	3.8900
		247.8330	3.8850
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		248.5000	3.8700
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		249.1670	3.8550
		249.5000	3.8450
		249.8330	3.8400
		250.1670	3.8300
		250.5000	3.8250
		250.8330	3.8150
		251.1670	3.8100
		251.5000	3.8000
		251.8330	3.7950
		252.1670	3.7850
		252.5000	3.7800
		252.8330	3.7700
		253.1670	3.7650
		253.5000	3.7550
		253.8330	3.7500
		254.1670	3.7400
		254.5000	3.7350
		254.8330	3.7250
		255.1670	3.7200
		255.5000	3.7100
		255.8330	3.7050
		256.1670	3.6950
		256.5000	3.6900
		256.8330	3.6800
		257.1670	3.6750
		257.5000	3.6650
		257.8330	3.6600
		258.1670	3.6500
		258.5000	3.6450
		258.8330	3.6350
		259.1670	3.6300
		259.5000	3.6200
		259.8330	3.6150
		260.1670	3.6050
		260.5000	3.6000
		260.8330	3.5900
		261.1670	3.5850
		261.5000	3.5750
		261.8330	3.5700
		262.1670	3.5600
		262.5000	3.5550
		262.8330	3.5450
		263.1670	3.5400
		263.5000	3.5300
		263.8330	3.5250
		264.1670	3.5150
		264.5000	3.5100
		264.8330	3.5000
		265.1670	3.4950
		265.5000	3.4850
		265.8330	3.4800
		266.1670	3.4700
		266.5000	3.4650
		266.8330

APPENDIX 5

LABORATORY CSTR SYSTEM DESCRIPTION AND MEAN RESIDENCE TIME DETERMINATIONS*

Schematic diagrams (Figures A5.1 and A5.2) show the elevation and plan of the completely stirred tank reactor (CSTR) used in the laboratory studies of $CaCO_3$ and $Mg(OH)_2$ precipitation from synthetic solutions and lime-treated secondary effluents. The dimensions for the two perspex units used in these tests are listed in Table A5.1.

The mean residence time of effluent being pumped through these two reactors was determined using sodium chloride as a tracer. The procedure was as follows : De-ionized water was pumped at a constant flow rate through the CSTR. At a moment designated as time, t = 0, a strong (± 10%) salt solution was pumped at a constant rate into the de-ionized feed-water line to the CSTR. This addition of salt was continued for a minimum of 3 residence times after which the addition was discontinued. Reactor effluent samples were taken at regular intervals and analysed for sodium by atomic absorption spectroscopy. Sampling extended over the full three residence times with salt addition and the subsequent three residence times without salt addition. Typical concentration versus time traces are shown in Figure A5.3.

Levenspiel (1972) has shown that the step input and step discontinuation of a tracer is given by the following relationships,

$$1-F = e^{-t/\bar{t}} \quad \text{..... (for input step) ... .} \quad \text{(A5.1)}$$

$$F = e^{-t/\bar{t}} \quad \text{..... (for discontinuation step) ... .} \quad \text{(A5.2)}$$

where $F = (C - C_i)/(C_m - C_o)$

.... (A5.3)

*See Chapter 3, p. 119 and Chapter 7, p. 330

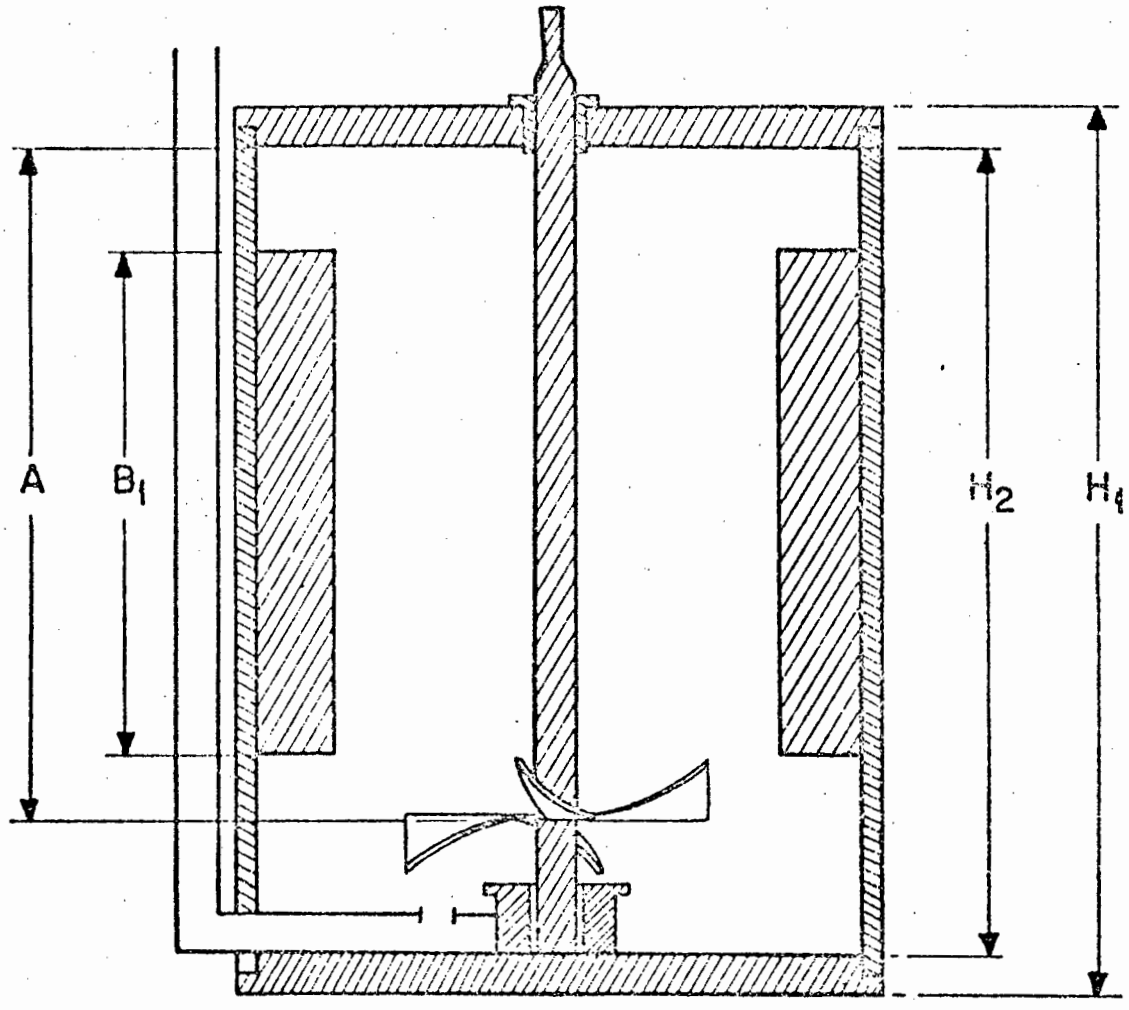

Figure A5.1. Elevation of CSTR used in bench-scale continuous precipitation experiments

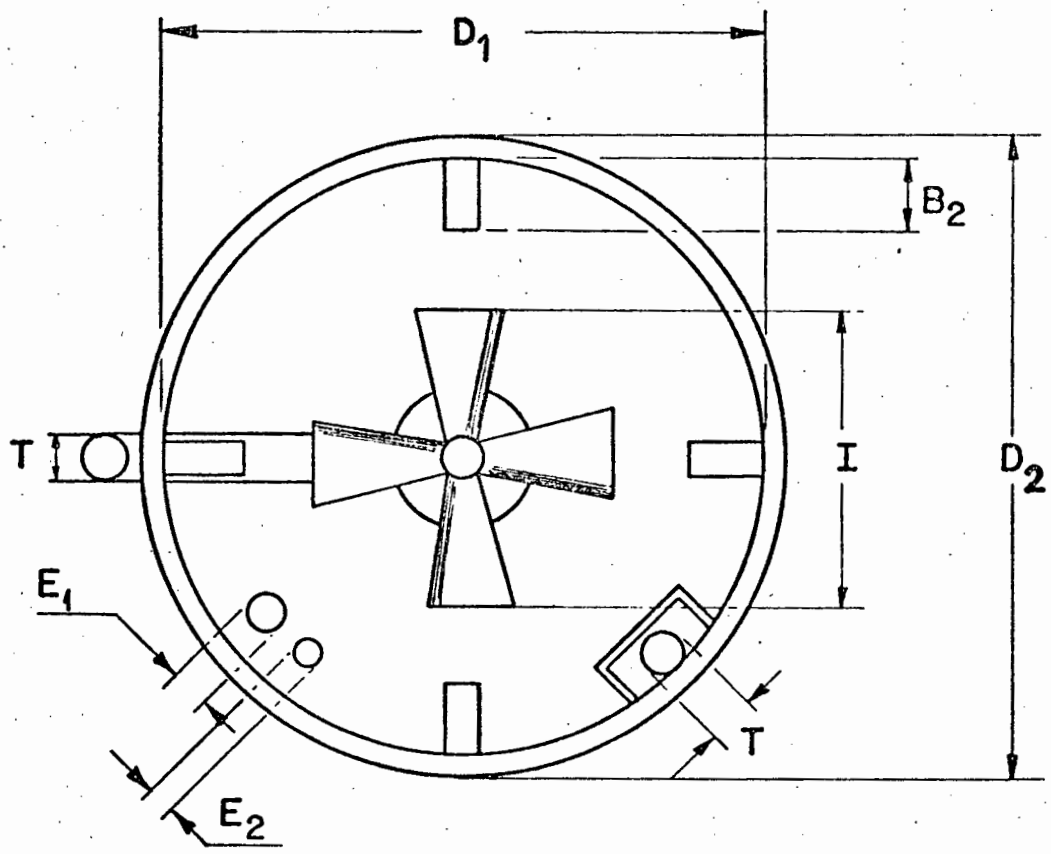

FIGURE A5.2 : Plan of CSTR

Table A5.1

Dimensions of CSTRs used in bench-scale precipitation experiments

Symbol	Symbol Identification**	Dimensions** Reactor R1 / Reactor R2	
A	Impeller depth	22,0	10,5
B_1	Baffle height	14,5	7,0
B_2	Baffle width	3,0	2,0
D_1	CSTR inner diameter	19,0	14,0
D_2	CSTR outer diameter	19,6	15,0
E_1	Hole for glass electrode	1,0	1,0
E_2	Hole for calomel electrode	0,8	0,8
H_1	CSTR outer height	30,0	15,5
H_2	CSTR inner height	28,0	13,0
I	Impeller diameter	13,5	8,0
T	Inlet and outlet pipe diameter	1,2	1,2
-	Volume (ℓ)	7,62	1,88

*See Figures A5.1 and A5.2

**All dimensions in cm, except volume (ℓ)

where C - Concentration of sodium at time = t

C_m - Concentration of sodium at time = infinity

C_o - Concentration of sodium at time = o

t - time (minutes)

$\bar{t}$ - mean residence time (minutes)

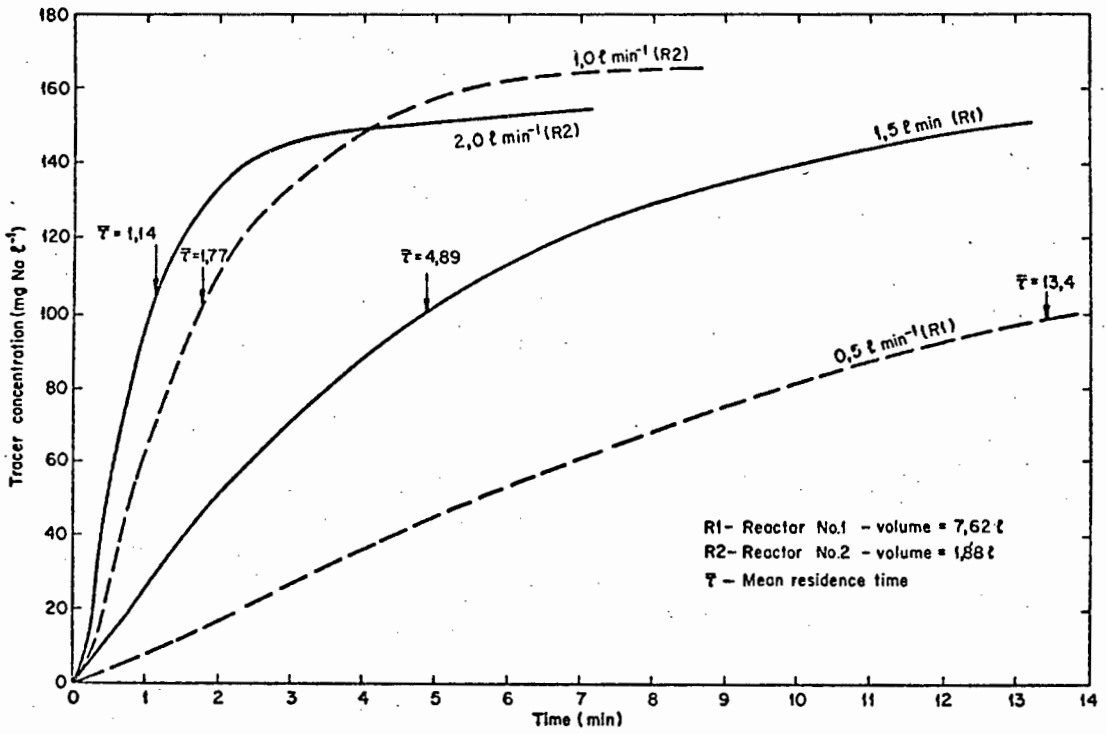

Figure A5.3. Plots of tracer concentration in reactor effluent as a function of period of tracer dosing

Taking the natural logarithm of Eq. (A5.1)

$$\ln(1-F) = -t/\bar{t} \qquad \ldots \quad (A5.4)$$

Therefore, a plot of ln(1-F) versus t should result in a straight line relationship, the slope of the line being equal to $-1/\bar{t}$ (see Figure A5.4).

Mean residence times were determined in the above described manner for the eight different residence times studied in this investigation. Table A5.2 lists the experimental results. The average mean residence time was taken as the arithmetic average between the mean residence time for the input step and discontinuation step. Correlation between the average mean residence time and the hydraulic retention time was excellent as illustrated in Figure A5.5, indicating near ideal mixing conditions in the reactors.

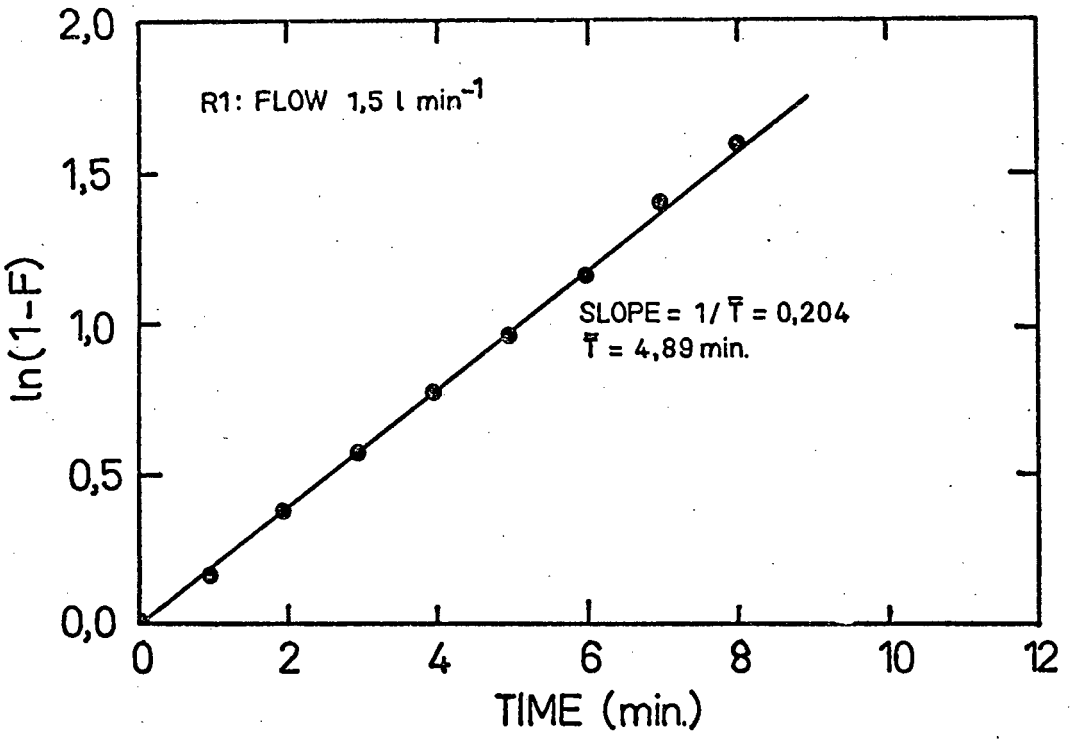

Figure A5.4. Kinetic plot used for the determination of CSTR mean residence time

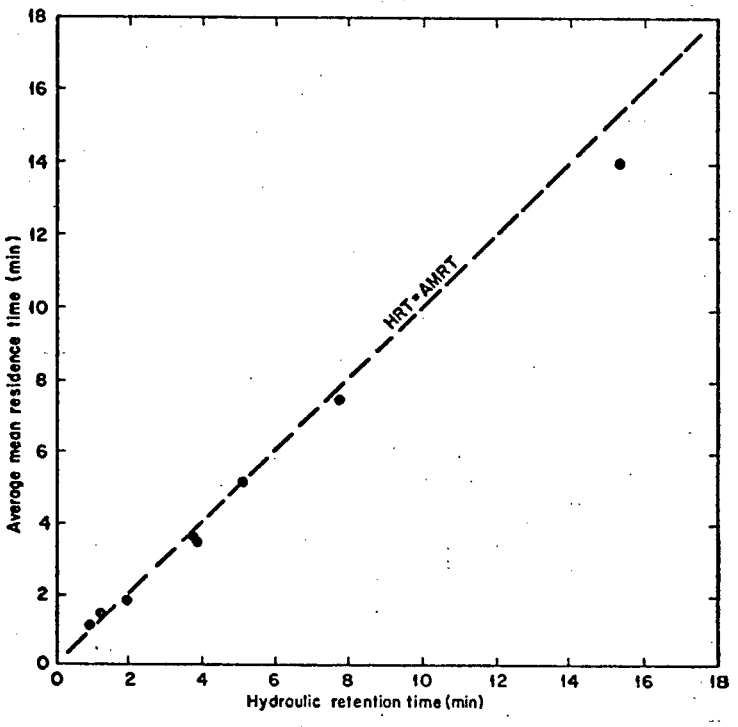

Figure A5.5. Comparison of hydraulic and experimentally determined average mean residence times for CSTRs

Table A5.2

Experimentally determined mean residence times for CSTRs for various flow rates

Solution flowrate	Hydraulic Residence Time	Mean Residence Time		Average Mean Residence Time
		Input step	Discontinuation step	
ℓ min $^{-1}$	min.	min.	min.	min.
		Reactor R2		
2,0	0,98	1,14	1,00	1,07
1,5	1,30	1,49	1,30	1,40
1,0	1,95	1,77	1,93	1,85
0,5	3,91	3,27	3,57	3,42
		Reactor R1		
2,0	3,84	3,67	3,45	3,56
1,5	5,13	4,87	5,44	5.17
1,0	7,69	8,04	6,85	7,45
0,5	15,38	13,40	14,60	14,00

APPENDIX 6

RAW DATA FOR EXPERIMENTS ON CONTINUOUS $CaCO_3$ PRECIPITATION FROM SYNTHETIC SOLUTIONS IN CSTR SYSTEMS*

Raw data collected during the investigation of continuous $CaCO_3$ precipitation from synthetic solutions in CSTR systems are listed below. The following codes are used,

HTE - Humus tank effluent (secondary effluent)
NA - Total dissolved sodium (mg ℓ^{-1} as Na)
CL - Total dissolved chlorides (mg ℓ^{-1} as Cl)
RN - Reactor identification
ID - Sample identification
HRT - Hydraulic retention time (min)**
MRT - Mean residence time (min)**
PHR - pH of reactor effluent
PHF - pH of filtered reactor effluent
ALK - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)
CAF - Residual total dissolved calcium (mg ℓ^{-1} as Ca)
CAT - Total calcium (mg ℓ^{-1} as Ca)

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* See Chapter 3, p. 119 and Chapter 6, p. 288

** All indicated retention times longer than 16 minutes are batch reaction times and are expressed in units of *hours*.

EXPERIMENT NO.= 1.

SYNTHETIC 'HTE+100 MG LIME/L'

NA= 200. K= 0. CL= 170. SO4= 0. NO3= 0.0 NO2= 0.0 ORG-C= 0. TOT.P= 0.0 TKN= 0.

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
2.	1.11	0.98	1.07	10.17	9.90	184.0	120.0	164.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.10	0.98	1.07	10.18	9.90	180.0	122.0	171.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.90	1.30	1.40	10.19	9.90	174.0	109.0	164.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.80	1.30	1.40	10.21	9.90	178.0	117.0	168.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.70	1.95	1.85	10.21	9.98	167.0	99.0	162.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.60	1.95	1.85	10.23	9.85	163.0	96.0	164.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.50	1.95	1.85	10.25	9.92	156.0	93.0	175.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.40	1.95	1.85	10.33	9.86	150.0	113.0	177.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.30	1.95	1.85	10.34	9.86	157.0	94.0	192.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.20	3.91	3.42	10.28	9.90	141.0	90.0	177.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.10	3.91	3.42	10.30	9.78	130.0	85.0	187.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.19	3.84	3.56	10.20	9.82	151.0	84.0	164.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.18	3.84	3.56	10.22	9.82	148.0	83.0	175.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.17	5.13	5.17	10.21	9.78	143.0	78.0	177.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.16	5.13	5.17	10.22	9.73	140.0	75.0	182.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.15	7.69	7.45	10.19	9.78	128.0	63.0	164.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.14	7.69	7.45	10.20	9.75	127.0	62.0	195.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.13	15.38	14.00	9.92	9.60	105.0	58.0	130.0	0.0	0.0	*****	0.0	0.	0.0
1.	1.12	15.38	14.00	9.95	9.68	105.0	60.0	139.0	0.0	0.0	*****	0.0	0.	0.0
2.	1.20	24.00	24.00	*****	9.25	89.0	22.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	1.21	100.00	100.00	*****	8.80	104.0	56.0	*****	0.0	0.0	*****	0.0	0.	0.0

EXPERIMENT NO.= 2.

SYNTHETIC 'HTE+50 MG LIME/L'

NA= 170. K= 0. CL= 120. SO4= 0. NO3= 0.0 NO2= 0.0 ORG-C= 0. TOT.P= 0.0 TKN= 0.

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
2.	2.08	0.98	1.07	9.62	9.58	198.0	135.0	149.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.07	0.98	1.07	9.66	9.62	201.0	139.0	151.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.06	1.30	1.40	9.45	9.42	197.0	131.0	153.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.05	1.30	1.40	9.50	9.40	192.0	132.0	150.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.06	1.95	1.85	9.20	9.38	196.0	135.0	148.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.03	1.95	1.85	9.22	9.37	195.0	135.0	147.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.02	3.91	3.42	9.25	9.22	167.0	125.0	144.0	0.0	0.0	*****	0.0	0.	0.0
2.	2.01	3.91	3.42	9.30	9.21	167.0	125.0	150.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.17	3.84	3.56	9.58	9.55	189.0	124.0	140.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.16	3.84	3.56	9.56	9.54	198.0	125.0	143.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.15	5.13	5.17	9.55	9.53	185.0	121.0	141.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.14	5.13	5.17	9.53	9.50	184.0	123.0	142.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.13	7.69	7.45	9.48	9.46	176.0	112.0	138.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.12	7.69	7.45	9.45	9.42	173.0	107.0	143.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.11	15.38	14.00	9.32	9.32	162.0	112.0	150.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.10	15.38	14.00	9.32	9.32	159.0	111.0	154.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.09	15.38	14.00	9.28	9.28	151.0	105.0	164.0	0.0	0.0	*****	0.0	0.	0.0
1.	2.20	24.00	******	*****	8.32	128.0	64.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	2.21	48.00	******	*****	8.46	122.0	60.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	2.22	24.00	******	*****	8.12	127.0	58.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	2.23	48.00	******	*****	8.18	116.0	52.0	*****	0.0	0.0	*****	0.0	0.	0.0

EXPERIMENT NO.= 3.

SYNTHETIC 'HTE+ 75 MG LIME/L'

NA= 185. K= 0. CL= 143. SO4= 0. NO3= 0.0 NO2= 0.0 ORG-C= 0. TOT.P= 0.0 TKN= 0.

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
2.	3.08	0.98	1.07	10.00	9.96	232.0	126.0	149.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.07	0.18	1.07	10.00	9.94	240.0	126.0	152.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.06	1.30	1.40	9.98	9.98	232.0	121.0	148.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.05	1.30	1.40	10.00	9.98	232.0	125.0	154.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.04	1.95	1.85	10.00	9.98	229.0	113.0	148.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.03	1.95	1.85	10.00	9.94	225.0	111.0	151.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.02	3.91	3.42	9.90	9.88	190.0	95.0	151.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.01	3.91	3.42	9.98	9.88	191.0	93.0	152.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.17	3.84	3.56	9.90	9.90	204.0	95.0	131.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.16	3.84	3.56	9.91	9.90	204.0	95.0	133.0	0.0	0.0	*****	0.0	0.	0.0
1.	3.15	5.13	5.17	9.90	9.90	193.0	87.0	130.0	0.0	0.0	*****	0.0	0.	0.0
1.	3.14	5.13	5.17	9.90	9.90	195.0	93.0	133.0	0.0	0.0	*****	0.0	0.	0.0
1.	3.13	7.69	7.45	9.90	9.88	189.0	72.0	136.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.12	7.69	7.45	9.88	9.88	187.0	73.0	142.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.11	15.38	14.00	9.76	9.73	156.0	63.0	151.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.10	15.38	14.00	9.72	9.71	155.0	61.0	155.0	0.0	0.0	*****	0.0	0.	0.0
2.	3.09	15.38	14.00	9.82	9.78	163.0	72.0	159.0	0.0	0.0	*****	0.0	0.	0.0
1.	3.18	48.00	******	*****	9.40	111.0	5.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	3.19	48.00	******	*****	9.32	112.0	5.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	3.20	24.00	******	*****	9.58	141.0	5.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	3.21	24.00	******	*****	9.60	142.0	5.0	*****	0.0	0.0	*****	0.0	0.	0.0

EXPERIMENT NO.= 4.

SYNTHETIC 'HTE+200 MG LIME/L'

NA= 262. K= 0. CL= 263. SO4= 0. NO3= 0.0 NO2= 0.0 ORG-C= 0. TOT.P= 0.0 TKN= 0.

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
2.	4.09	0.98	1.07	10.80	10.55	233.0	182.0	236.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.08	0.98	1.07	10.80	10.65	232.0	170.0	235.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.07	1.30	1.40	10.78	10.67	206.0	149.0	195.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.05	1.30	1.40	10.78	10.64	208.0	146.0	201.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.04	1.95	1.85	10.76	10.63	181.0	112.0	192.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.03	1.95	1.85	10.75	10.67	186.0	121.0	207.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.02	3.90	3.42	10.67	10.50	136.0	107.0	228.0	0.0	0.0	*****	0.0	0.	0.0
2.	4.01	3.91	3.42	10.68	10.50	129.0	117.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	4.17	3.84	3.56	10.76	10.70	162.0	109.0	233.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.16	3.84	3.56	10.77	10.70	161.0	110.0	245.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.15	5.13	5.17	10.77	10.62	153.0	101.0	234.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.14	5.13	5.17	10.77	10.62	155.0	104.0	247.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.13	7.69	7.45	10.76	10.60	144.0	88.0	259.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.12	7.69	7.45	10.77	10.58	142.0	89.0	274.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.11	15.38	14.00	10.67	10.48	105.0	82.0	323.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.10	15.38	14.00	10.67	10.50	100.0	78.0	313.0	0.0	0.0	*****	0.0	0.	0.0
1.	4.18	24.00	******	*****	10.41	72.0	14.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	4.19	24.00	******	*****	10.40	64.0	7.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	4.20	48.00	******	*****	10.40	64.0	8.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	4.21	48.00	******	*****	10.42	64.0	6.0	*****	0.0	0.0	*****	0.0	0.	0.0

EXPERIMENT NO.= 5.

SYNTHETIC 'HTE+300MG LIME/L'

NA= 325. K= 0. CL= 360. SO4= 0. NO3= 0.0 NO2= 0.0 ORG-C= 0. TOT.P= 0.0 TKN=

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
2.	5.08	0.99	1.07	11.32	11.23	296.0	228.0	296.0	0.0	0.0	*****	0.0	0.	0.0
2.	5.07	0.98	1.07	11.32	11.22	298.0	221.0	294.0	0.0	0.0	*****	0.0	0.	0.0
2.	5.06	1.30	1.40	11.31	11.24	269.0	200.0	279.0	0.0	0.0	*****	0.0	0.	0.0
2.	5.05	1.30	1.40	11.30	11.22	255.0	191.0	286.0	0.0	0.0	*****	0.0	0.	0.0
2.	5.04	1.95	1.85	11.31	11.20	253.0	165.0	259.0	0.0	0.0	*****	0.0	0.	0.0
2.	5.03	1.95	1.85	11.34	11.26	251.0	162.0	260.0	0.0	0.0	*****	0.0	0.	0.0
1.	5.16	3.84	3.56	11.31	13.22	301.0	163.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.15	3.84	3.56	11.33	11.32	228.0	164.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.14	5.13	5.17	11.33	11.33	210.0	154.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.13	5.13	5.17	11.32	11.26	214.0	147.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.12	7.69	7.45	11.32	11.31	197.0	124.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.11	7.69	7.45	11.32	11.28	193.0	130.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.10	15.38	14.00	11.26	11.18	152.0	122.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.09	15.38	14.00	11.26	11.17	139.0	99.0	*****	0.0	0.0	*****	0.0	0.	0.0
1.	5.17	24.00	******	*****	11.08	94.0	25.0	*****	0.0	0.0	*****	0.0	0.	0.0
2.	5.18	24.00	******	*****	11.08	90.0	16.0	*****	0.0	0.0	*****	0.0	0.	0.0

APPENDIX 7

DERIVATION OF RELATIONSHIP BETWEEN REACTOR RADIUS AND HEIGHT FOR THE MINIMUM AREA TO VOLUME RATIO*†

In an effort to minimize scale formation, precipitation reactors must be designed to have minimal exposed area to the supersaturated water. For this reason cylindrical reactors are preferred with a radius to height ratio of one.

DERIVATION

Area, A, of cylinder exposed to effluent is,

$$A = \Pi r^2 + 2\Pi rh \quad \ldots\ (A7.1)$$

where r - cylinder radius
h - water head in cylinder

Cylinder volume, V, is,

$$V = \Pi r^2 h \quad \ldots\ (A7.2)$$

It is required to minimize A for any fixed V,

$$V(\text{constant}) = \Pi r^2 h \quad \ldots\ (A7.3)$$

$$h = V/\Pi r^2 \quad \ldots\ (A7.4)$$

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*See Chapter 3, p. 120

†The author is indebted to Dr M Nattrass for the mathematical derivation.

Substituting in Eq. (A7.1)

$$A = \Pi r^2 + 2V/r \quad \ldots\ldots \quad (A7.5)$$

$$\frac{dA}{dr} = 2\Pi r - \frac{2V}{r^2} = o \quad \ldots\ldots \quad (A7.6)$$

$$2\pi r = 2V/r^2 \quad \ldots\ldots \quad (A7.7)$$

$$r^3 = V/\Pi \quad \ldots\ldots \quad (A7.8)$$

$$r = V/\Pi r^2 \quad \ldots\ldots \quad (A7.9)$$

Eq. (A7.4) and Eq. (A7.9) are identical, therefore

$$r = h \text{ for A minimized} \quad \ldots\ldots \quad (A7.10)$$

EXAMPLE

Common practice in the design of water treatment reactors is to choose the reactor diameter (d) and height (h) to be approximately equal, i.e.

$$h = d = 2r \quad \ldots\ldots \quad (A7.11)$$

Therefore, area exposed to effluent is

$$A = \Pi r^2 + 2\Pi rh$$
$$= \Pi r^2 + 2\Pi r\,(2r)$$
$$A = 5\Pi r^2 \quad .... \quad (A7.12)$$

If the design criterion given by Eq.(A7.10) is used, the area exposed to effluent is,

$$A = \Pi r^2 + 2\Pi rh$$
$$= \Pi r^2 + 2\Pi r(r)$$
$$A = 3\Pi r^2 \quad .... \quad (A7.13)$$

Assume a $10m^3$ reactor has to be designed. The radius for such a reactor on the basis of Eq. (A7.11) can be calculated as follows,

$$V = \Pi r^2 h = \Pi^{r2}(2r) = 10$$
$$r = (10/2\Pi)^{1/3} = 1,168m \quad .... \quad (A7.14)$$

The area exposed to the effluent will be (Eq. A7.12)

$$A = 5\Pi r^2 = 21,43\ m^2 \quad .... \quad (A7.15)$$

If the design criterion given by Eq. (A7.10) is used, the radius for such a reactor is calculated as follows,

$$V = \Pi r^2 h = \Pi r^2 (r) = 10$$

$$r = (10/\Pi)^{1/3} = 1,471 \quad \ldots. \quad (A7.16)$$

Area exposed to the effluent will be Eq. A7.13),

$$A = 3\Pi r^2 = 20,39\ m^2 \quad \ldots. \quad (A7.17)$$

Therefore, 4,8% less area for the same volume is exposed to the supersaturated solution by designing h = r rather than h = 2r. This consideration with others, such as mixing, structural and cost considerations will determine the final optimal reactor geometry.

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APPENDIX 8

RAW DATA FOR EXPERIMENTS ON BATCH REACTION OF LIME WITH SECONDARY EFFLUENT*

Raw data collected during the investigation of batch reaction of lime with secondary effluent are listed below. The following codes are used,

Time - Time interval after the addition of lime (min)
$Temp_R$ - Temperature of batch reactor solution (^oC)
pH_R - pH of batch reactor solution
$Temp_F$ - Temperature of filtered batch reactor solution (^oC)
pH_F - pH of filtered batch reactor solution
Alk - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)
Ca_F - Residual total dissolved calcium (mg ℓ^{-1} as Ca)
Mg_F - Residual total dissolved magnesium (mg ℓ^{-1} as Mg)
Ca_T - Total calcium (mg ℓ^{-1} as Ca)
Mg_T - Total magnesium (mg ℓ^{-1} as Mg)

The analyses given for time, t = o, correspond to secondary effluent without any lime addition.

*See Chapter 4, p. 168

EXPERIMENT 1

LIME DOSAGE = 226 mg ℓ^{-1}

Time	$Temp_R$	pH_R	$Temp_F$	pH_F	Alk	Ca_F	Mg_F	Ca_T	Mg_T
0	25,0	7,50	25,0	7,88	137	41	19,7	46	19,8
1	-	10,16	-	-	-	50	14,2	-	-
2	-	10,24	-	-	-	65	15,4	-	-
3	-	10,29	-	-		51	14,7	-	-
4	-	10,31	-	-	-	52	15,3	-	-
5	-	10,33	-	-	-	49	14,5	-	-
7	-	10,34	-	-	-	47	14,4	-	-
10	-	10,33	-	-	-	48	15,0	-	-
15	-	10,32	-	-	-	42	14,7	-	-
30	25,6	10,29	25,8	10,02	138	39	15,2	112	18,8
60	26,7	10,27	26,6	9,92	136	38	15,0	108	19,0
90	27,8	10,24	26,2	9,90	136	37	15,0	116	19,6

EXPERIMENT 2

LIME DOSAGE = 310 mg ℓ^{-1}

Time	$Temp_R$	pH_R	$Temp_F$	pH_F	Alk	Ca_F	Mg_F	Ca_T	Mg_T
0	27,0	7,50	26,0	7,88	137	41	19,7	46	19,8
1		11,00				67	16,0		
2		11,04				52	14,4		
3		11,04				47	14,5		
4		11,03				46	14,2		
5		11,01				46	14,3		
7		10,95				40	13,3		
10		10,90				39	12,7		
15		10,85				36	12,0		
30	27,2	10,83	26,2	10,72	109	36	11,4	220	20,
60	28,0	10,82	26,0	10,62	101	35	10,0	176	19,
90	27,0	10,71	26,6	10,58	94	34	9,0	144	19,

EXPERIMENT 3

LIME DOSAGE = 365 mg ℓ^{-1}

Time	$Temp_R$	pH_R	$Temp_F$	pH_F	Alk.	Ca_F	Mg_F	Ca_T	Mg_T
0	27,0	7,60	26,5	7,98	133			41	19,5
1		11,14				45	14,0		
2		11,15				65	13,1		
3		11,15				49	11,6		
4		11,12				48	11,2		
5		11,08				48	10,3		
7		10,96				45	9,5		
10		10,94				45	8,4		
15		10,92				40	7,5		
30	27,4	10,90	26,0	10,85	101	42	6,3	160	19,
60	28,0	10,88	26,4	10,80	91	40	3,9	160	18,
90	28,2	10,87	26,6	10,80	89	41	4,4	164	18,

EXPERIMENT 4

LIME DOSAGE = 427 mg ℓ^{-1}

Time	$Temp_R$	pH_R	$Temp_F$	pH_F	Alk	Ca_F	Mg_F	Ca_T	Mg_T
0	25,0	7,60	25,0	7,98	133	41	19,3	41	19,3
1		11,23				62	13,0		
2		11,28				72	12,7		
3		11,28				53	10,5		
4		11,27				51	10,1		
5		11,27				46	9,2		
7		11,27				43	10,0	(?)	
10		11,26				43	3,2	(?)	
15		11,25				42	2,5	(?)	
30	25,7	11,25	25,5	11,03	108	43	6,0	176	18,0
60	26,6	11,23	25,8	11,00	95	41	4,7	180	18,8
90	27,3	11,20	26,2	10,98	89	41	4,1	192	18,8

EXPERIMENT 5

LIME DOSAGE = 504 mg ℓ^{-1}

Time	$Temp_R$	pH_R	$Temp_F$	pH_F	Alk	Ca_F	Mg_F	Ca_T	Mg_T
0	26,5	7,60	26,5	7,98	133	41	19,5	41	19,5
1		11,42				78	7,3		
2		11,45				77	5,7		
3		11,46				65	4,3		
4		11,46				62	3,7		
5		11,46				64	3,0		
7		11,45				60	2,7		
10		11,45				59	1,8		
15		11,45				57	1,6		
30	27,4	11,45	27,0	11,22	139	64	0,8	208	19,1
60	27,8	11,43	26,9	11,20	139	64	0,5	208	19,6
90	27,0	11,41	26,9	11,20	136	62	0,4	208	20,0

EXPERIMENT 6

LIME DOSAGE = 671 mg ℓ^{-1}

Time	$Temp_R$	pH_R	$Temp_F$	pH_F	Alk	Ca_F	Mg_F	Ca_T	Mg_T
0	22,8	7,60	25,4	7.98	133	41	19,3	41	19,5
1		11,66				91	5,5		
2		11,71				87	2,8		
3		11,70				85	2,3		
4		11,69				93	2,2		
5		11,64				75	1,8		
7		11,61				79	1,7		
10		11,59				84	1,4		
15		11,58				78	1,2		
30	24,2	11,55	25,4	11,49	198	92	0,5	260	19,2
60	25,8	11,53	25,9	11,50	200	92	0,5	264	19,2
90	26,8	11,50	26,3	11,50	203	92	0,5	264	19,2

APPENDIX 9

PROGRAMME EXPDA1*

Programme EXPDA1 calculates the species concentration, Ca^{+2}, CO_3^{-2}, HCO_3^-, H_2CO_3, $CaCO_3^o$, $CaCO_3(S)$, $CaHCO_3^+$, H^+ and OH^- from initial reactant concentrations and experimentally measured pH values.

The theory concerning the calculation of species has been set out in Chapter 3, and hence only the calculation technique is discussed in this section.

Calculation of Equilibrium Constants

The equilibrium and solubility constants are temperature dependent. The dependence of K_1, K_2 K_w and K_{sp} have been reported in the literature (Shadlowsky and MacInnes, 1935; Harned and Scholes (1941); Harned and Hamer, 1933),

$$pK_1 = (17052/TA) + [215,21 * \log(TA)] - (0,12675 * TA) - 545,56 \quad \ldots (A9.1)$$

$$pK_2 = (2902,39/TA) + (0,02379 * TA) - 6,498 \quad \ldots (A9.2)$$

$$pK_w = (4787/TA) + [7,1321 * \log(TA)] + (0,01037 * TA) - 22,801 \quad \ldots (A9.3)$$

$$pK_{sp} = 0,01183 * TS + 8,03 \quad \ldots (A9.4)$$

where TA = Absolute temperature (^oK)
TS = Temperature (^oC)

Equilibrium and the solubility constants are calculated using equations (A9.1), (A9.2), (A9.3), (A9.4) and the experimental temperature.

The thermodynamic dissociation constants, $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$ are temperature dependent, but only values at 25°C have been quoted in the literature (Garrels and Christ, 1965). In the calculation sequence these constants are taken not to vary with temperature and are taken to be

$$K_{CaCO_3^o} = 0,000631$$

$$K_{CaHCO_3^+} = 0,055$$

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*See Chapter 3, p. 101

Calculation of Ionic Equilibrium at the Initial State of the Experiment

On mixing solutions of $NaHCO_3$, NaOH and $CaCl_2$, ionic equilibrium is set up within milliseconds. The calculation sequence for determining the species concentration for ionic equilibrium, before calcium carbonate starts to precipitate is as follows,

1. Development of Equations for Calculation Sequence

(a) From equations (3.23), (3.12), (3.13), (3.10)

$$Ca_T = [Ca^{+2}] + [CaHCO_3^+] + [CaCO_3^o]$$

$$= [Ca^{+2}] + \frac{[Ca^{+2}][HCO_3^-] \cdot f_D}{K_{CaHCO_3^+}} + \frac{[Ca^{+2}][CO_3^{-2}] \cdot f_D}{K_{CaCO_3^o}}$$

$$= [Ca^{+2}] \left[1 + \frac{[HCO_3^-] \cdot f_D}{K_{CaHCO_3^+}} + \frac{K_2 \cdot f_D}{K_{CaCO_3^o}} \cdot \frac{[HCO_3^-]}{[H^+]} \right] \quad \ldots (A9.5)$$

(b) From equations (3.21), (3.23)

$$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] + [CaHCO_3^+] + [CaCO_3^o]$$

$$= [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] + Ca_T - [Ca^{+2}]$$

$$\therefore \quad [CO_3^{-2}] = [Ca^{+2}] + C_T - [H_2CO_3] - [HCO_3^-] - Ca_T \quad \ldots (A9.6)$$

2. Calculation Sequence

(a) Assume a pH value.

(b) Calculate $[H^+]$ from equation (3.16)

$$\log[H^+] = - pH - \log f_M$$

where pH is the assumed value and f_M is initially assumed to be 0,912.

(c) Assume a value for $[HCO_3^-]$

(d) Calculate $[Ca^{+2}]$ from equation (A9.5)

$$[Ca^{+2}] = Ca_T \Big/ \left[1 + \frac{[HCO_3^-]\, f_D}{K_{CaHCO_3^+}} + \frac{K_2 \cdot f_D}{K_{CaCO_3^o}} \cdot \frac{[HCO_3^-]}{[H^+]}\right]$$

where Ca_T, $K_{CaHCO_3^+}$, K_{CaCO_3}, K_2 are known values, $[H^+]$ is a calculated value, f_D is an initially assumed value (say 0,692) and $[HCO_3^-]$ is an assumed value.

(e) Calculate $[H_2CO_3]$ from equation (3.9)

$$[H_2CO_3] = [H^+][HCO_3^-] \cdot f_M^2/K_1$$

where K_1 is a known value, $[H^+]$ is a calculated value, and f_M and $[HCO_3^-]$ are initially assumed values.

(f) Calculate $[CO_3^{-2}]$ from equation (A9.6)

$$[CO_3^{-2}] = [Ca^{+2}] + C_T - [H_2CO_3] - [HCO_3^-] - Ca_T$$

where C_T and Ca_T have known values, $[Ca^{+2}]$ and $[H_2CO_3]$ have calculated values, and $[HCO_3^-]$ has an assumed value.

(g) Calculate $[CaHCO_3^+]$ from equation (3.12)

$$[CaHCO_3^+] = [Ca^{+2}][HCO_3^-] \cdot f_D/K_{CaHCO_3^+}$$

where $K_{CaHCO_3^+}$ has a known value, $[Ca^{+2}]$ has calculated value and $[HCO_3^-]$ and f_D have initially assumed values.

(h) Calculate $[OH^-]$ from equation (3.11)

$$[OH^-] = K_w/([H^+] * f_M^2)$$

where K_w has a known value, $[H^+]$ has a calculated value and f_M has an initially assumed value.

(i) Calculate $[CaCO_3^o]$ from equation (3.13)

$$[CaCO_3^o] = [Ca^{+2}][CO_3^{-2}] \cdot f_D^2 / K_{CaCO_3^o}$$

where $K_{CaCO_3^o}$ has a known value, $[Ca^{+2}]$ and $[CO_3^{-2}]$ are calculated values and f_D has an initially assumed value.

(j) Calculate I from equation (3.11)

$$I = 0,5 * ([Na^+] + [H^+] + 4[Ca^{+2}] + [CaHCO_3^+] + [Cl^-] + [OH^-] + [HCO_3^-] + 4[CO_3^{-2}]$$

where $[Na^+]$, $[Cl^-]$ have known values; $[Ca^{+2}]$, $[H^+]$, $[CaHCO_3^+]$, $[OH^-]$ and $[CO_3^-]$ have calculated values, and $[HCO_3^-]$ has an initially assumed value.

(k) Calculate F(I) from equation (3.19)

$$F(I) = ([I^{1/2}/\{1 + I^{1/2}\}] - 0,3\ I)$$

where I has a calculated value.

(l) Calculate f_M and f_D from equations (3.17) and (3.18)

$$\log f_M = - 0,5 * F(I)$$

$$\log f_D = - 2,0 * F(I)$$

(m) Calculate $[HCO_3^-]$ from equation (3.20)

$$[HCO_3^- = [Na^+] + 2[Ca^{+2}] + [H^+] + [CaHCO_3] - [Cl^-] - [OH^-] - 2[CO_3^-]$$

where $[Na^+]$ and $[Cl^-]$ have known values; $[Ca^{+3}]$, $[H^+]$, $[CaHCO_3^+]$, $[OH^-]$ and $[CO_3^{-2}]$ have calculated values.

All the unknown species concentrations in solution have now been calculated based on the initial assumed concentrations. In addition, using the calculated values, $[HCO_3^-]$ is now evaluated. This will very likely differ from the initially assumed value. If the value of $[HCO_3^-]_{ASS}$ is larger than $[HCO_3^-]_{CALC}$ its value must be decreased to give a better approximation to $[HCO_3^-]_{CALC}$, and vice versa.

The magnitude of the decrease in $[HCO_3^-]_{ASS}$ is established as follows. If $[HCO_3^-]_{CALC}$ is larger than $[HCO_3^-]_{ASS}$, the value of $[HCO_3^-]_{ASS}$ is replaced by a value 1,1 * $[HCO_3^-]_{ASS}$ and the above series of calculations is repeated. The values obtained for the species concentrations in the first calculation cycle are used where applicable.

If $[HCO_3^-]_{CALC}$ is smaller than $[HCO_3^-]_{ASS}$ a test must be made to ascertain if their difference (X) is less than 0,0001 * $[HCO_3^-]_{ASS}$, i.e. less than 0,01% of $[HCO_3^-]_{ASS}$. If this is true, $[HCO_3^-]_{ASS}$ is assumed to be the value which gives a self-consistent result for the equations of state. If this is not true the value of $[HCO_3^-]_{ASS}$ is reduced by 0,1 * X and a new cycle of calculations of species concentrations is made.

This procedure is continued until the value of $[HCO_3^-]_{ASS}$ is smaller than $[HCO_3]_{CALC}$. At this point in the calculation sequence 0,1 * X is added to $[HCO_3]_{ASS}$ and 0,01 * X is subtracted from this value. This procedure is followed until the incremental change applied to $[HCO_3^-]_{ASS}$ is less than 0,0001 * $[HCO_3^-]_{ASS}$.

A series of self-consistent values of $[H^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{-2}]$, $[Ca^{+2}]$, $[CaHCO_3^+]$, $[CaCO_3^o]$, pH and I have now been calculated for an assumed pH. The calculated and assumed pH values are now compared. If there is a difference, the assumed value is increased (or decreased) by 0,001 and the above calculation sequence is repeated. This procedure is repeated until the assumed and calculated pH values are within 0,002 of each other.

A series of self-consistent values of all the species concentrations, pH and I have now been calculated for the ionic equilibrium state just after mixing the reactants. These species concentrations are utilized in the subsequent calculations and will be referred to as follows: for $[H^+]$ at ionic equilibrium at t = 0, $[H^+]_i$; for $[OH^-] = [OH^-]_i$; for $[Ca^{+2}] = [Ca^{+2}]_i$, etc.

Calculation of All the Species Concentrations During Precipitation

In Chapter 3 it was shown that all the species concentrations during the precipitation process, at any particular time t, may be calculated if the initial species concentrations at t = 0, the equilibrium constants, the thirteen equations of state and the experimentally measured pH at time t are known.

A table of species concentrations for series pH values (~1000), between pH values 10,000 and 8,500, is constructed in the following section of the program. This is done as follows:

1. Development of Equations Necessary for the Creation of the Abovementioned Table

Equation for $[HCO_3^-]$ from equation (3.27)

$$[HCO_3^-] = [Ca^{+2}]_i - [Ca^{+2}] + [H_2CO_3] + [CO_3^{-2}] - ([H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{-2}]_i) \quad \ldots (A9.7)$$

2. Calculation Sequence

The table is created by starting with the initial species concentrations (t = 0) as the first set of values. The second set of values is generated by assuming that the calcium value has decreased by 0,1 mg/l (0,1 * 10^{-5} moles. l^{-1}). A new set of corresponding species concentrations is calculated as follows:

(a) Calculate $[HCO_3^-]$ from equation (A9.7)

$$[HCO_3^-] = [Ca^{+2}]_i - [Ca^{+2}] + [H_2CO_3] + [CO_3^{-2}] - ([H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{-2}]_i)$$

where $[Ca^{+2}]_i$, $[Ca^{+2}]$, $[H_2CO_3]_i$, $[HCO_3^-]_i$, $[CO_3^{-2}]_i$ are known and previously calculated values; $[H_2CO_3]$ and $[CO_3^{-2}]$ are initially assumed to be equal to $[H_2CO_3]_i$ and $[CO_3^{-2}]_i$ respectively.

(b) Calculate $[H^+]$ from equation (3.10)

$$[H^+] = K_2 \cdot [HCO_3^-]/([CO_3^{-2}] \cdot f_D)$$

where K_2 has a known value; $[HCO_3^-]$ has a calculated value; $[CO_3^{-2}]$ and f_D have initially assumed values.

(c) Calculate $[H_2CO_3]$ from equation (3.9)

$$[H_2CO_3] = [H^+].[HCO_3^-] \cdot f_M^2/K_1$$

where K_1 has a known value; $[H^+]$ and $[HCO_3^-]$ have calculated values; and f_M has an initially assumed value.

(d) Calculate $[OH^-]$ from equation (3.11)

$$[OH^-] = K_w/([H^+] \cdot f_M^2)$$

where K_w has a known value; $[H^+]$ a calculated value and f_M an initial assumed value.

(e) Calculate pH from equation (3.16)

$$pH = - \log ([H^+] \cdot f_M)$$

where $[H^+]$ has a calculated value and f_M an initially assumed value.

(f) Calculate $CaCO_3^o$ from equation (3.13)

$$[CaCO_3^o] = [Ca^{+2}].[CO_3^{-2}] \cdot f_D^2/K_{CaCO_3^o}$$

where $[Ca^{+2}]$ and $K_{CaCO_3^o}$ are known values; $[CO_3^{-2}]$ and f_D are initially assumed values.

(g) Calculate $CaHCO_3^+$ from equation (3.12)

$$[CaHCO_3^+] = [Ca^{+2}].[HCO_3^-] f_D/K_{CaHCO_3^+}$$

where $[Ca^{+2}]$ and $K_{CaHCO_3^+}$ are known values; $[HCO_3^-]$ is a calculated value, and f_D is an initial assumed value.

(h) Calculate I from equation (3.22)

$$I = 0,5 * ([CaHCO_3^+] + [Na^+] + [H^+] + 4[Ca^{+2}] + [Cl^-] + [OH^-] + [HCO_3^-] + 4[CO_3^{-2}])$$

where $[Ca^{+2}]$, $[Na^+]$ and $[Cl^-]$ have known values; $[HCO_3^-]$, $[CaHCO_3^+]$ and $[OH^-]$ have calculated values; $[CO_3^{-2}]$ has an initial assumed value.

(i) Calculate F(I) from equation (3.19)

$$F(I) = \{[I^{1/2}/(1 + I^{1/2})] - 0,3\ I\}$$

where I is a calculated value.

(j) Calculate $[CO_3^{-2}]$ from equation (3.20)

$$[CO_3^{-2}] = 0,5 * \{2[Ca^{+2}] + [CaHCO_3^+] + [Na^+] + [H^+] - [Cl^-] - [OH^-] - [HCO_3^-]\}$$

where $[Ca^{+2}]$, $[Na^+]$, $[Cl^-]$ have known values; $[CaHCO_3^+]$, $[H^+]$, $[OH^-]$ and $[HCO_3^-]$ have calculated values.

All the unknown species concentrations in solution have now been calculated, based on the initial assumed concentrations. In addition, using the calculated values, $[CO_3^{-2}]$ is now evaluated. This will very likely differ from the initial assumed value. If the value of $[CO_3^{-2}]_{ASS}$ is larger than $[CO_3^{-2}]_{CALC}$, its value must be decreased to give a better approximation to $[CO_3^{-2}]_{CALC}$, and vice versa.

The magnitude of the decrease (or increase) is $1,0 * 10^{-7}$ (moles. l^{-1}) and the above calculation is repeated until the magnitudes of $[CO_3^{-2}]_{ASS}$ and $[CO_3^{-2}]_{CALC}$ are within $2,0 * 10^{-7}$ moles. l^{-1} of each other. A series of self-consistent values of all the species and the pH have now been calculated. These values are now entered in the table as the second set. The whole process is repeated, approximately 1000 times to produce a table consisting of a 1000 sets of species concentrations.

By means of the above method the species concentrations in solution can be calculated to any number of significant figures. However, the accuracy of the answer depends on the accuracy of K_1, K_2, K_w, $K_{CaCO_3^o}$, $K_{CaHCO_3^+}$, $[Na^+]$, $[Cl^-]$, C_T and Ca_T.

The concentration of $CaCO_3(S)$ precipitated is calculated as follows:

$$[CaCO_3(S)] = [Ca^{+2}]_i + [CaHCO_3^+]_i + [CaCO_3^o] - \{[Ca^{+2}] + [CaHCO_3^+] + [CaCO_3^o]\}$$

$$Ca\ CO_3(S) = 5{,}0 \times 10^4 \times [Ca\ CO_3\ (S)]$$

and the proposed function for heterogeneous $CaCO_3$ precipitation is calculated as follows:

$$FUNCTION = CaCO_3(S).\ \{[Ca^{+2}].[CO_3^{-2}] - K_{sp}/f_D^2\}$$

These two values are also placed in the abovementioned table.

The experimentally measured pH values and times of measurement are now read into the computer. Each experimental pH is now compared with the array of pH values in the table, and the corresponding pH and species concentrations are printed as output data.

In conclusion, programme EXPDA1 has the following INPUT DATA, concentrations of reactants, temperature, seed crystal concentration and experimental pH and time of pH measured. It calculates all the species concentrations in solution corresponding to the measured pH-values, and the function proposed to be linearly related to the rate of precipitation.

Programme EXPDA1 was tested as follows:

One value for experimentally measured pH is used as input data. The calculated values of $[H^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{-2}]$, $[Ca^{+2}]$, $[CaCO_3^o]$, $[CaHCO_3^+]$, f_M and f_D were used to calculate the thermodynamic equilibrium constants K_1, K_2, K_w, $K_{CaHCO_3^+}$ and $K_{CaCO_3^o}$ and agreed to within 0,1 % of the literature values.

```
C      PROGRAM   EXPDA1
C*************************************************************************
C      THIS PROGRAM CALCULATES SPECIES CONCENTRATIONS ( CA++, CO3-- )
C      AND FUCTION  (M*(CA*CO3-KSP/FD2))
C      FROM INITIAL REACTANT CONCENTRATIONS AND EXPERIMENTAL
C      PH VALUES.
C*************************************************************************
C
C      NNUM=NO. OF DATA SETS(I2)
C
C      DATA SET
C
C      FIRST DATA CARD : IDENT   (A4).
C      IDENT IS THE EXPERIMENT IDENTIFICATION NUMBER.
C
C      SECOND DATA CARD :   NAHCO3,NAOH,CACL2.  (3E10.4).
C      NAHCO3 IS THE SODIUMBICARBONATE CONCENTRATION (MOLES/L) T=0.
C      NAOH IS THE SODIUM HYDROXIDE CONCENTRATION (MOLES/L) T=0.
C      CACL2 IS THE CALCIUM CHLORIDE CONCENTRATION (MOLES/L) T=0.
C
C      THIRD DATA CARD :   TS.   (F5.1).
C      TS IS THE TEMPERATURE IN DEGREES CELCIUS.
C
C      FORTH DATA CARD : EQPH   (F6.2).
C      EQPH= PH AT T=0.
C
C      FIFTH DATA CARD: CACOSI   (F10.4).
C      CACOSI IS THE INITIAL SEED CRRYSTAL CONCENTRATION IN MG/L.
C
C      EXPERIMENTAL DATA SET :   PHEXP(N),TIMEXP(N).   (2F10.4)
C      PHEXP(N) IS THE EXPERIMENTAL PH VALUE, DIRECT INSTRUMENT READING.
C      TIMEXP(N) IS THE TIME WHEN PHEXP WAS READ.
C      TERMINATE INPUT OF EXPERIMENTAL DATA SET WITH  999. IN COLS 1 - 4
C
C      NEXT DATA CARD :   AMINPH,AFACT  (2F10.0)
C      AMINPH= MINIMUM PH ON RECORDER RANGE.
C      AFACT= SCALE FACTOR(=0.08 FOR METRIC PAPER ON HEWLITT PACKARD).
C
C      NEXT DATA CARD :       NOPLOT   (I1)
C      IF NOPLOT=0    NO PLOT IS PLOTTED
C      IF NOPLOT=1     A PLOT IS PLOTTED
C
C      NEXT DATA CARD :      MINUS  (I2)
C      MINUS= NUMBER OF POINTS WHICH MUST BE NEGLECTED IN LLSF.
C
C      NEXT DATA CARD:  AFOOP  (2A4).
C      AFOOP= EXPERIMENT IDENTIFICATION NUMBER.
C*************************************************************************
      DIMENSION    HD(1000),OHD(1000),CO3D(1000),HCO3D(1000),
     1H2CO3D(1000),CACOOD(1000),CAHCOO(1000),UD(1000),FD(1000),
     2CAD(1000),CACOST(1000),R(1000),CACOSF(1000),CCO3D(1000)
      DIMENSION    PHD(1000),T(1000),TC(1000)
      DIMENSION    RORC(1000)
      DIMENSION    PHEXP(200),TIMEXP(200)
      DIMENSION    FUNCTD(1000)
      DIMENSION    RATE(200),CAEXP1(1000),FUNCT1(1000)
      DIMENSION   CADFIT(100)
      DIMENSION    PHEXPS(100)
      DIMENSION   X(100),Y(100),Z(100)
      DIMENSION    FM1(1000),FD1(1000),CASEXP(1000)
      DIMENSION  FUNT(250)
      REAL   NA,NAHCO3,NAOH,K1,K2,KW,KCO3O,KHCO3,KCACO3,KSP,KOH
      COMMON/MIPLOT/ A,B,RR,KEND
      N=1
      M=3
      READ(N,1001)   NNUM
1001  FORMAT(I2)
      DO 1002  JNUM=1,NNUM
      READ(N,234)  IDENT
234   FORMAT(A4)
      WRITE(M,235)   IDENT
235   FORMAT(1H1,'EXPERIMENT  NO.',A4,///)
      READ(N,1)    NAHCO3,NAOH,CACL2
1     FORMAT(3E10.4)
      WRITE(M,2)   NAHCO3,NAOH,CACL2
```

```
2     FORMAT(1H ,'NAHCO3 = ',E10.4,4X,'NAOH = ',E10.4,4X,
     1'CACL2 = ',E10.4,///)
      NA=NAHCO3+NAOH
      CT=NAHCO3
      CAT=CACL2
      CL=2.*CACL2
      READ(N,3)    TS
3     FORMAT(F10.4)
      WRITE(M,4)   TS
4     FORMAT(1H ,'TEMPERATURE = ',F10.1,2X,'DEGREES CELCIUS',///)
C*****************************************************************
C     CALCULATION OF EQUILIBRIUM CONSTANTS.
C*****************************************************************
      TA=TS+273.15
      PK1=(17052./TA)+215.21*ALOG(TA)/ALOG(10.)-(.12675*TA)-545.56
      K1=1./10.**PK1
      PK2=(2902.39/TA)+(.02379*TA)-6.498
      K2=1./10.**PK2
      PKW=(4787.3/TA)+(7.1321*ALOG(TA)/ALOG(10.))+(.01037*TA)-22.801
      KW=1./10.**PKW
      PKSPX=0.01183*TS+8.03
      KSP=1./10.**PKSPX
      KOH=0.0502
      KCO3O=0.000631
      KHCO3=0.055
      PKOH=ALOG10(KOH)-(1190./(2.3*1.987))*(1./TA-1./298.15)
      PKCO3O=ALOG10(KCO3O)-(3130./(2.3*1.987))*(1./TA-1./298.15)
      PKHCO3=ALOG10(KHCO3)-(6331./(2.3*1.987))*(1./TA-1./298.15)
      KOH=10.**PKOH
      KCO3O=10.**PKCO3O
      KHCO3=10.**PKHCO3
      WRITE(M,5)   K1,K2,KW,KHCO3,KSP,KCO3O
5     FORMAT(1H ,'K1 = ',E10.4,4X,'K2 = ',E10.4,4X,'KW = ',E10.4,
     14X,'KCAHCO3+ = ',E10.4,4X,'KSP =',E10.4,4X,'KCACO3O = ',E10.4,
     2///)
C*****************************************************************
C     CALCULATION OF SPECIES CONCETRATION AT IONIC
C     EQUILIBRIUM, T=0 ,WHEN NO CACO3 HAS AS YET PRECIPITATED.
C*****************************************************************
      READ(N,833)    EQPH
833   FORMAT(F6.2)
      WRITE(M,834)   EQPH
934   FORMAT(1H ,'EQPH = ',F6.2,//)
212   QQQQ=0.
      H2CO3=0.
      FMXX=0.912
      FDXX=0.692
      NTEL8=0
506   RUN10=1.
      RUN11=1.
      HCO3=0.3*NAHCO3
      CHCO3=0.0
      PH=EQPH+QQQQ
      AH=-PH-ALOG10(FMXX)
      AH=-AH
      H=1./10.**AH
      NTEL7=0
307   NTEL7=NTEL7+1
      IF(NTEL7.EQ.500)        GO TO 100
      CA=CAT/(1.+(HCO3*FDXX/KHCO3)+(K2*FDXX*HCO3/(KCO3O*H)))
      CO3=K2*HCO3/(H*FDXX)
      IF(CO3-0.0)    350,350,351
350   ZZZZ=HCO3
      WRITE(M,107)
107   FORMAT(1H ,'CO3 IS NEGATIVE, MAKE HCO3=HCO3-0.00001')
      HCO3=ZZZZ-0.00001
      GO TO 307
351   CONTINUE
      H2CO3=H*HCO3*(FMXX**2.)/K1
      CAHCO3=CA*HCO3*FDXX/KHCO3
      CACO3O=CA*CO3*(FDXX**2.)/KCO3O
      OH=KW/(H*(FMXX**2.))
      CHCO3=NA+2.*CA+H+CAHCO3-CL-OH-2.*CO3
      U=0.5*(NA+H+4.*CA+CAHCO3+CL+OH+HCO3+4.*CO3)
      F=((SQRT(U)/(1.+SQRT(U)))-0.3*U)
      AFMXX=0.5*F
      FMXX=1./10.**AFMXX
      AFDXX=2.*F
      FDXX=1./10.**AFDXX
```

```
      RUN101=2.
      IF(RUN10-RUN101)    300,300,305
300   IF(HCO3-CHCO3)    303,304,305
303   Q1=0.01*HCO3
      ZHCO3=HCO3
      HCO3=ZHCO3+Q1
      GO TO 307
305   RUN10=3.
      RUN111=2.
      IF(RUN11-RUN111)    308,308,309
308   Q2=HCO3-CHCO3
      RUN11=3.
309   IF(HCO3-CHCO3)    403,311,405
405   HCO3PO=HCO3
403   Q6=0.1*Q2
      Q7=HCO3-Q6
      Q8=0.0001*HCO3
      IF(Q2-Q8)    311,311,325
325   IF(HCO3-CHCO3)    406,311,408
408   HCO3=Q7
      GO TO 307
406   HCO3=HCO3PO-0.01*Q2
      ZQ2=Q2
      Q2=0.01*ZQ2
      GO TO 307
304   CONTINUE
311   CONTINUE
      NTEL8=NTEL8+1
      IF(NTEL8.EQ.500)        GO TO 103
      CCO3=CA+CT-HCO3-H2CO3-CAT
      IF(CCO3.LT.0)      GO TO 108
      H=K2*HCO3/(CCO3*FDXX)
      CPH=-ALOG10(H)+0.5*F
      QQQ=PH-CPH
      QQQA=ABS(QQQ)
      IF(QQQA-0.002)    501,501,502
502   IF(PH-CPH)    503,504,505
503   XQY=QQQQ
      QQQQ=XQY-0.001
      GO TO 506
505   YQX=QQQQ
      QQQQ=YQX+0.001
      GO TO 506
501   CONTINUE
504   CONTINUE
      WRITE(M,79)  CA,CO3,PH,U
79    FORMAT(1H ,'CA=',E10.4,5X,'CO3=',E10.4,5X,'PH=',E10.4,5X,
     .'IONC STRENGTH=',F10.6,//)
      WRITE(M,80)  CACO30,CAHCO3,H,OH
80    FORMAT(1H ,'CACO30=',E10.4,5X,'CAHCO3=',E10.4,5X,'H=',E10.4,5X,
     .'OH=',E10.4,//)
      WRITE(M,81)  HCO3,H2CO3
81    FORMAT(1H ,'HCO3=',E10.4,5X,'H2CO3=',E10.4,//)
      WRITE(M,82)  FMXX,FDXX
82    FORMAT(1H ,'FM=',F6.3,5X,'FD=',F6.3,//)
C*****************************************************************
C     TEST IF EQUILIBRIUM VALUES HAVE BEEN CALCULATED TO REQUIRED
C     ACCURACY
C*****************************************************************
      WRITE(M,112)
112   FORMAT(1H ,'PERCENTAG ERRORS OF CALCULATED VALUES = ',/)
      TCT=H2CO3+HCO3+CO3+CAHCO3+CACO30
      PCT=(CT-TCT)*100./CT
      TCAT=CA+CAHCO3+CACO30
      PCAT=(CAT-TCAT)*100./CAT
      TKCO3=CA*CO3*(FDXX**2.)/CACO30
      PKCO3=(KCO30-TKCO3)*100./KCO30
      TKHCO3=CA*HCO3*FDXX/CAHCO3
      PKHCO3=(KHCO3-TKHCO3)*100./KHCO3
      PCT=ABS(PCT)
      PCAT=ABS(PCAT)
      PKCO3=ABS(PKCO3)
      PKHCO3=ABS(PKHCO3)
      WRITE(M,113) PCT,PCAT,PKCO3,PKHCO3
113   FORMAT(1H ,'CT=',E10.4,5X,'CAT=',E10.4,5X,'KCO3=',E10.4,5X,'KHCO3=
     .',E10.4,//)
807   CONTINUE
      HD(1)=H
```

```
      OHD(1)=OH
      CO3D(1)=CO3
      HCO3D(1)=HCO3
      H2CO3D(1)=H2CO3
      CACOOD(1)=CACO3O
      CAHCOD(1)=CAHCO3
      UD(1)=U
      FD(1)=F
      CAD(1)=CA
      PHD(1)=CPH
      WRITE(M,806)   PHD(1)
806   FORMAT(' CALCULATED EQUILIBRIUM PH = ',F6.2,//)
      READ(N,21)     CACOSI
21    FORMAT(F10.4)
      WRITE(M,22)    CACOSI
22    FORMAT(1H ,'CACO3 SEED CRYSTAL CONCENTRATION = ',F10.4,///)
      FUNCTD(1)=CACOSI*(CA*CO3-KSP/(FDXX**2.))
      CACOSF(1)=0.0
C*********************************************************************
C     CREATE A TABLE WITH PH- AND CORRESPONDING SPECIES
C     CONCENTRATIONS VALUES.
C*********************************************************************
      DO   23   N=2,1000
      NN=N-1
      CAD(N)=CAD(NN)-0.000001
      CO3D(N)=CO3D(NN)-0.000001
      H2CO3D(N)=H2CO3D(NN)
      FD(N)=FD(NN)
      RUN3=1.
      RUN4=1.
      AA4=CAD(N)
      CCCC=0.0
      NT=1
995   XXXZ=CO3D(N)+CCCC
28    AA3=CO3D(N)
      IF(NT.EQ.1) GO TO 888
      HCO3D(N)=H2CO3D(1)+HCO3D(1)+CO3D(1)-H2CO3D(N)-CO3D(N)-CAD(1)
     1+CAD(N)
      NT=2
      GO TO 889
888   HCO3D(N)=HCO3D(NN)
889   CONTINUE
      AA2=HCO3D(N)
      IF(K2.LT.0.0)      GO TO 711
      IF(AA3.LT.0.0)     GO TO 712
      IF(AA2.LT.0.0)     GO TO 713
      AH=ALOG10(K2)-ALOG10(AA3)+ALOG10(AA2)+2.*FD(N)
      AH=-AH
      HD(N)=1./10.**AH
      AA7=HD(N)
      IF(AA7.LT.0.0)     GO TO 714
      IF(K1.LT.0.0)      GO TO 715
      AH2CO3=ALOG10(AA7)+ALOG10(AA2)-ALOG10(K1)-FD(N)
      AH2CO3=-AH2CO3
      H2CO3D(N)=1./10.**AH2CO3
      AA1=H2CO3D(N)
      IF(KW.LT.0.0)      GO TO 716
      AOH=ALOG10(KW)-ALOG10(AA7)+FD(N)
      AOH=-AOH
      OHD(N)=1./10.**AOH
      AA8=OHD(N)
      PHD(N)=-ALOG10(AA7)+0.5*FD(N)
      IF(AA4.LT.0.0)     GO TO 717
      IF(KCO3O.LT.0.0)   GO TO 718
      ACACOO=ALOG10(AA4)+ALOG10(AA3)-ALOG10(KCO3O)-4.*FD(N)
      ACACOO=-ACACOO
      CACOOD(N)=1./10.**ACACOO
      AA5=CACOOD(N)
      IF(KHCO3.LT.0.0)   GO TO 719
      ACAHCO=ALOG10(AA4)+ALOG10(AA2)-ALOG10(KHCO3)-2.*FD(N)
      ACAHCO=-ACAHCO
      CAHCOD(N)=1./10.**ACAHCO
      AA6=CAHCOD(N)
      U=0.5*(CAHCOD(N)+NA+HD(N)+4.*CAD(N)+CL+OHD(N)+HCO3D(N)
     1+4.*CO3D(N))
      FD(N)=(SQRT(U)/(1.+SQRT(U)))-0.3*U
      FM1(N)=0.5*FD(N)
      FM1(N)=1./10.**FM1(N)
```

```
      FD1(N)=2.0*FD(N)
      FD1(N)=1./10.**FD1(N)
      CCO3D(N)=.5*(CAHCOD(N)+NA+HD(N)+2.*CAD(N)-CL-OHD(N)-HCO3D(N))
      IF(CCO3D(N)-0.0)    900,900,901
  901 CONTINUE
      CO3D(N)=XXXZ
      CCC=CO3D(N)-CCO3D(N)
      CCCA=ABS(CCC)
      IF(CCCA-0.0000002)     990,990,991
  991 IF(CO3D(N)-CCO3D(N))    992,993,994
  992 ZXQY=CCCC
      CCCC=ZXQY+0.0000001
      GO TO  995
  994 ZXYQ=CCCC
      CCCC=ZXYQ-0.0000001
      GO TO 995
  990 CONTINUE
  993 CONTINUE
C*************************************************************************
C     TEST IF THERE IS MORE THAN 0.5 PERCENT DISCREPENCY BETWEEN
C     GIVEN AND CALCULATED VALUES OF KCACO30 AND KCAHCO3+.
C*************************************************************************
      TKCO3=CAD(N)*CO3D(N)*(FD1(N)**2.)/CACOOD(N)
      PKCO3=(KCO30-TKCO3)*100./KCO30
      TKHCO3=CAD(N)*HCO3D(N)*FD1(N)/CAHCOD(N)
      PKHCO3=(KHCO3-TKHCO3)*100./KHCO3
      PKCO3=ABS(PKCO3)
      PKHCO3=ABS(PKHCO3)
      IF(PKCO3.GT.0.5)  GO TO 739
      IF(PKHCO3.GT.0.5) GO TO 739
      GO TO 734
  739 WRITE(M,740)  N,PKCO3,PKHCO3
  740 FORMAT(1H ,'N=',I3,5X,'PERCENTAGE ER.:KCACO30=',F10.3,',',2X,'KCAH
     .CO3+=',F10.3,//)
  734 CONTINUE
      CAT0=CAD(1)+CAHCOD(1)+CACOOD(1)
      CATN=CAD(N)+CAHCOD(N)+CACOOD(N)
      CACOSF(N)=CAT0-CATN
      CACOSF(N)=100000.*CACOSF(N)
      CACOST(N)=CACOSI+CACOSF(N)
      AF2=2.*FD(N)
      F2=(1./10.**AF2)**2.
      PKSF2=KSP/F2
      FUNCTD(N)=(CACOST(N))*((CAD(N) )*(CO3D(N))-PKSF2)
      IF(FUNCTD(N).LT.0.0)   GO TO 731
   23 CONTINUE
  731 N=N-1
      WRITE(M,791)   CACOSF(N)
  791 FORMAT(1H ,'CACO3(S) PPT. AT TIME INFINITY =',F10.2,//)
  900 MMM=N
  216 CONTINUE
      N=1
      M=3
      K=0
  220 K=K+1
      READ(N,223)              TIMEXP(K),PHEXP(K)
  223 FORMAT(2F10.4)
      IF (TIMEXP(K).NE.999.) GO TO 220
      NPHTIM=K-1
C*************************************************************************
C     GENERATE PH-VALUES FROM RECORDER READINGS.
C*************************************************************************
      READ(N,741)  AMINPH,AFACT
  741 FORMAT(2F10.0)
      DO 742 K=1,NPHTIM
      PHEXP(K)=AMINPH+AFACT*PHEXP(K)
  742 CONTINUE
      ERPH=  PH-PHEXP(1)
      WRITE(M,737) ERPH
  737 FORMAT(1H ,'PHO-PH(T=0)=',F10.3,//)
      DO  792  I=1,NPHTIM
  792 PHEXP(I)=PHEXP(I)+ERPH
      WRITE(M,221)   NPHTIM
  221 FORMAT(1H ,'NUMBER  OF  EXPERIMENTAL  PH  AND  TIME  VALUES = ',
     1I2,///)
      READ(N,820)   NOPLOT
  820 FORMAT(I1)
      DO   222   K=1,NPHTIM
      X(K)=TIMEXP(K)
```

```
      Y(K)=PHEXP(K)
222   CONTINUE
225   CONTINUE
      NDIM=NPHTIM
      WRITE(M,235)   IDENT
      WRITE(M,793)   ERPH
793   FORMAT(1H ,'PH=PHEXP + ERPH(',F10.3,')',//)
      WRITE(M,451)
451   FORMAT(1H ,3X,'TIME',8X,'PH',6X,'PH(SMOOTH)',//)
      CALL    SG13(X,Y,Z,NDIM,IER)
      LDIM=NDIM-1
      DO   452   K=2,LDIM
      PHEXPS(K)=Z(K)
452   CONTINUE
      DO   453   K=2,LDIM
      WRITE(M,450)      TIMEXP(K),PHEXP(K),PHEXPS(K)
450   FORMAT(3F10.4)
      PHEXP(K)=PHEXPS(K)
453   CONTINUE
C*************************************************************************
C     FIND  PH-VALUES  WHICH  CORRESPOND  TO  THE  EXPERIMENTAL  PH
C*************************************************************************
      DO   227   N=1,NPHTIM
      DO   228   K=2,MMM
      KK=K-1
      IF(PHEXP(N)-PHD(KK))   229,230,230
230   CAEXP=CAD(KK)
      CO3EXP=CO3D(KK)
      REXP=R(KK)
      CAOEXP=CAOOD(KK)
      CAHEXP=CAHOD(KK)
      CASEXP(N)=CAOSF(KK)
      FUNCTE=FUNCTD(KK)
      CAEXP1(N)=CAD(KK)
      FUNCT1(N)=FUNCTD(KK)
      CADFIT(N)=CAD(KK)
      FM11=FM1(KK)
      FD11=FD1(KK)
      GO TO 227

229   CONTINUE
228   CONTINUE
227   CONTINUE
710   CONTINUE
      WRITE(M,235)   IDENT
      WRITE(M,599)
599   FORMAT(1H ,2X,'TIME',11X,'RATE',11X,'M*(CA*CO3-KSP/FD2)',
     .5X,'CACO3(S)',5X,'PH',10X,'FUNTO',5X,'FUNT',///)
      DO   600   K=1,NPHTIM
      K2=K+4
      K3=K+2
      DELCA=CADFIT(K)-CADFIT(K2)
      DELTIM=TIMEXP(K)-TIMEXP(K2)
      RATE(K3)=DELCA/DELTIM
600   CONTINUE
      KEND=NPHTIM-4
      NDIM=NPHTIM-4
      CALL SG13(TIMEXP,RATE,Z,NDIM,IER)
      WRITE(4,235)  IDENT
      K9=KEND-4
      WRITE(4,949)  K9
949   FORMAT(I3)
      DO    602   K=5,KEND
      RATE(K)=-Z(K)
      FUNT(K)=FUNCT1(K)/CACOST(K)
      FUNTO=FUNCTD(1)
      WRITE(M,601)    TIMEXP(K),RATE(K),FUNCT1(K),CASEXP(K),
     .PHEXP(K),FUNTO,FUNT(K)
601   FORMAT(F10.4,5X,E10.4,13X,E10.4,4X,F10.2,5X,F10.2,5X,2(E10.4,
     .5X))
      WRITE(4,931)   CACOSI,CASEXP(K),FUNT(K)
931   FORMAT(2(F10.2,5X),E10.4)
602   CONTINUE
      DO   604   K=5,KEND
      WRITE(4,933)    RATE(K)
933   FORMAT(E10.4)
      KK=K-4
      TIMEXP(KK)=TIMEXP(K)
      RATE(KK)=RATE(K)
```

```
      FUNCT1(KK)=FUNCT1(K)
  604 CONTINUE
      KEND=KEND-4
      READ(1,607)   MINUS
  607 FORMAT(I2)
      WRITE(3,608)  MINUS
  608 FORMAT(1H ,//,' N = ',I2)
  821 N=1
      M=3
      NDIM=KEND-MINUS
      DO   606   I=1,NDIM
      TIMEXP(I)=RATE(MINUS+I)
  606 PHEXP(I)=FUNCT1(MINUS+I)
      CALL LEAST(PHEXP,TIMEXP,NDIM,A,B,SA,SB,RR,TT)
      IF(NOPLOT.EQ.0)    GO TO 822
      DO 605 I=1,KEND
      II=I+KEND
      RATE(II)  =A+B*FUNCT1(I)
  605 FUNCT1(II)=FUNCT1(I)
      NDIM=KEND+KEND
C              THE EXPERIMENTAL DATA ARE SYMBOL PLOTTED AND THE BEST STRAIGHT
C LINE THROUGH THE POINTS (OBTAINED FROM LEAST) IS DRAWN
      CALL PLOT(FUNCT1,RATE,NDIM)
  822 WRITE(M,235)   IDENT
      WRITE(M,4)  TS
      WRITE(M,603)    B,SB,A,SA,RR,TT
  603 FORMAT(1H ,' RATE CONSTANT = ',F10.4,10X,' STANDARD DEVIATION = ',
     1F10.4,//,' INTERSECTION ON RATE AXIS = ',E10.4,'     STANDARD DEVI
     2ATION = ',E10.4,//,' R-FACTOR = ',F10.4,//,' T-FACTOR = ',F10.4)
      B1=B*(1.053**(25.0-TS))
      WRITE(M,794)  B1
  794 FORMAT(1H ,'RATE CONSTANT(25 C) =',F10.4,//)
      GO TO 105
  100 WRITE(M,101)
  101 FORMAT(1H ,'NTEL7=500')
      GO TO 105
  103 WRITE(M,104)
  104 FORMAT(1H ,'NTEL8=500')
      GO TO 105


  108 WRITE(M,109)
  109 FORMAT(1H ,'CCO3 IS NEGATIVE')
  105 CONTINUE
      GO TO 729
  711 WRITE(M,720)       K2
  720 FORMAT(1H1,'K2=',E11.4)
      GO TO 729
  712 WRITE(M,721)       AA3
  721 FORMAT(1H1,'AA3=',E11.4)
      GO TO 729
  713 WRITE(M,722)       AA2
  722 FORMAT(1H1,'AA2=',E11.4)
      GO TO 729
  714 WRITE(M,723)       AA7
  723 FORMAT(1H1,'AA7=',E11.4)
      GO TO 729
  715 WRITE(M,724)       K1
  724 FORMAT(1H1,'K1=',E11.4)
      GO TO 729
  716 WRITE(M,725)       KW
  725 FORMAT(1H1,'KW=',E11.4)
      GO TO 729
  717 WRITE(M,726)       AA4
  726 FORMAT(1H1,'AA4=',E11.4)
      GO TO 729
  718 WRITE(M,727)       KCO30
  727 FORMAT(1H1,'KCO30=',E11.4)
      GO TO 729
  719 WRITE(M,728)       KHCO3
  728 FORMAT(1H1,'KHCO=',E11.4)
      GO TO 729
  729 CONTINUE
 1002 CONTINUE
C     LAST STATEMENT NO. IS 742
      STOP
      END
```

```
      SUBROUTINE LEAST(X,Y,N,A,B,SA,SB,R,T)                              00000100
      DIMENSION X(1),Y(1)
      SUMX=0                                                             00000300
      SUMY=0                                                             00000400
      DO 10 I=1,N                                                        00000500
      SUMX=SUMX+X(I)                                                     00000600
   10 SUMY=SUMY+Y(I)                                                     00000700
      XBAR=SUMX/N                                                        00000800
      YBAR=SUMY/N                                                        00000900
      SUMX=0                                                             00001000
      SUMY=0                                                             00001100
      SUMX2=0                                                            00001200
      SUMY2=0                                                            00001300
      SUMXY=0                                                            00001400
      DO 20 I=1,N                                                        00001500
      XX=X(I)-XBAR                                                       00001600
      YY=Y(I)-YBAR                                                       00001700
      SUMX=SUMX+XX                                                       00001800
      SUMY=SUMY+YY                                                       00001900
      SUMX2=SUMX2+XX*XX                                                  00002000
      SUMY2=SUMY2+YY*YY                                                  00002100
   20 SUMXY=SUMXY+XX*YY                                                  00002200
      B=SUMXY/SUMX2                                                      00002300
      A=YBAR-B*XBAR                                                      00002400
      R=ABS(SUMXY)/SQRT(SUMX2*SUMY2)                                     00002500
      T=R/SQRT((1-R*R)/(N-2))                                            00002600
      SUMY=0                                                             00002700
      DO 30 I=1,N                                                        00002800
   30 SUMY=SUMY+(Y(I)-A-B*X(I))**2                                       00002900
      SB2=SUMY/SUMX2                                                     00003000
      SA2=(SUMX2/N+XBAR*XBAR)*SB2                                        00003100
      SA=SQRT(SA2)                                                       00003200
      SB=SQRT(SB2)                                                       00003300
      RETURN                                                             00003400
      END


      SUBROUTINE PLOT(X,Y,NPT)
      REAL*8 AFDOP
      REAL*4 HOOFOP(9),X(  1),Y(  1),                XAS(5),YAS(3)
      COMMON/MIPLOT/A,B,RR,NDIM
      DATA HOOFOP/'HETE','ROGE','NEOU','S CA','CO3 ','PREC','IPIT',
     .   'ATIO','N.  '/,
     .                    XAS/'M(CA','*CO3','-KSP','/FD2',')   '/,
     .YAS/'D(CA','++)/','DT  '/,  INDIC/0/, XX/0.0/
      ISIM=11
      IF (INDIC.EQ.1) GO TO 75
      READ(1,30) AFDOP
   30 FORMAT(A8)
C  DEFINIEER PLOT AREA
      INDIC=1
      CALL PLASGN(70,99)
   75 CALL UNITDF(39.37,39.37)
      CALL PLOTDF(XX,0.,0.,0.,2.,2.,27.5,17.5,29.5,20.5,255)
      XX=30.
C  SKRYF OPSKRIFTE
      CALL VSYMBL(3.5,16.1,0.5,0.3,0.,0.,0.,HOOFOP,36)
      YV=14.
      CALL VSYMBL(22.,YV,.35,.20,0.,0.,0.,ISIM   ,-1)
      YV=YV-.15
      CALL VSYMBL(22.5,YV,.35,.20,0.,0.,0.,' - ',3)
      CALL CSYMBL(AFDOP, 8)
   79 YV=YV-1.
      CALL VSYMBL(22.0,YV,.2,.14,0.,0.,0.,'RATE CONST.=',12)
      CALL RNUMBR(25.31,YV,.2,.14,0.,0.,B,'F2.4')
      YV=YV-.75
      CALL VSYMBL(22.0,YV,.2,.14,0.,0.,0.,'INTERSECTION ON',15)
      YV=YV-.5
      CALL MSYMBL(22.0,YV,'RATE AXIS=',10)
      CALL RNUMBR(24.81,YV,.2,.14,0.,0.,   A,'E4.2')
      YV=YV-.75
      CALL VSYMBL(22.0,YV,.2,.14,0.,0.,0.,'R-FACTOR =',10)
      CALL RNUMBR(24.81,YV,.2,.14,0.,0.,RR,'F1.4')
      YV=YV-.75
      CALL VSYMBL(22.0,YV,.2,.14,0.,0.,0.,'N=',2)
      NDIM=NDIM/2
```

```
      CALL INUMBR(22.56,YV,.2,.14,0.,0.,   NDIM,0)
C  BEREKEN MINIMUMS EN INKREMENTE
   80 J=NPT+1
      X(J)=0.
      Y(J)=0.
      XMAX=X(1)
      YMAX=Y(1)
      DO 86 I=2,NPT
      IF (XMAX.LT.X(I)) XMAX=X(I)
      IF (YMAX.LT.Y(I)) YMAX=Y(I)
   86 CONTINUE
      J=J+1
      X(J)=XMAX/18.
      Y(J)=YMAX/12.
C  TREK ASSE
   85 XV=18.
      CALL PSCALE(X,Y,NPT,18.,39.37,12.,39.37,3)
      CALL RAXIS (3.5,3.5,0.,3.5,3.5,90.,XAS,-20,YAS,12,27)
      NPP=NPT/2
      CALL RLINE(X,Y,1,NPP,-1,ISIM    ,0.0)
      I1=NPP+1
      CALL RLINE(X,Y,I1,NPP,0,ISIM,0.0)
      WRITE(3,110)
  110 FORMAT('0HAPPINESS IS A PLOT WHICH WORKED'//)
      RETURN
      END
```

EXPERIMENT NO.1C

NAHCO3 = 0.1983E-02 NAOH = 0.9480E-03 CACL2 = 0.2046E-02

TEMPERATURE = 24.7 DEGREES CELCIUS

K1 = 0.4298E-06 K2 = 0.4653E-10 KW = 0.9878E-14 KCAHCO3+ = 0.5441E-01 KSP =0.4762E-08
KCACO30 = 0.6276E-03
EQPH = 9.80

CA=0.1546E-02 CO3=0.4048E-03 PH=0.9788E 01 IONC STRENGTH= 0.007995

CACO30=0.4787E-03 CAHCO3=0.2119E-04 H=0.1779E-09 OH=0.6645E-04

HCO3=0.1076E-02 H2CO3=0.3723E-06

FM= 0.912 FD= 0.693

PERCENTAG ERRORS OF CALCULATED VALUES =
CT=0.7615E-01 CAT=0.7966E-04 KCO3=0.1966E-02 KHCO3=0.9448E-03

CALCULATED EQUILIBRIUM PH = 9.79

CACO3 SEED CRYSTAL CONCENTRATION = 50.0000

N=425 PERCENTAGE ER.:KCACO3O= 0.975, KCAHCO3+= 0.000

N=426 PERCENTAGE ER.:KCACO3O= 1.069, KCAHCO3+= 0.000

N=427 PERCENTAGE ER.:KCACO3O= 1.182, KCAHCO3+= 0.000

CACO3(S) PPT. AT TIME INFINITY = 90.21

PHO-PH(T=O)= 0.016

NUMBER OF EXPERIMENTAL PH AND TIME VALUES = 60

PH=PHEXP + ERPH(0.016)

TIME	PH	PH(SMOOTH)
0.1000	9.7840	9.7827
0.2000	9.7760	9.7760
0.3000	9.7680	9.7680
0.4000	9.7600	9.7613
0.5000	9.7560	9.7560
0.6000	9.7520	9.7507
0.7000	9.7440	9.7453
0.8000	9.7400	9.7387
0.9000	9.7320	9.7320
1.0000	9.7240	9.7240
1.1000	9.7160	9.7173
1.2000	9.7120	9.7107
1.3000	9.7040	9.7040
1.4000	9.6960	9.6960
1.5000	9.6880	9.6880
1.6000	9.6800	9.6800

1.7000	9.6720	9.6720
1.8000	9.6640	9.6627
1.9000	9.6520	9.6520
2.0000	9.6400	9.6413
2.1000	9.6320	9.6320
2.2000	9.6240	9.6240
2.3000	9.6160	9.6147
2.4000	9.6040	9.6053
2.5000	9.5960	9.5947
2.6000	9.5840	9.5853
2.7000	9.5760	9.5760
2.8000	9.5680	9.5667
2.9000	9.5560	9.5560
3.0000	9.5440	9.5457
3.2000	9.5280	9.5280
3.4000	9.5120	9.5093
3.6000	9.4880	9.4907
3.8000	9.4720	9.4693
4.0000	9.4480	9.4507
4.2000	9.4320	9.4293
4.4000	9.4080	9.4093
4.6000	9.3880	9.3880
4.8000	9.3680	9.3667
5.0000	9.3440	9.3467
5.2000	9.3280	9.3253
5.4000	9.3040	9.3067
5.6000	9.2880	9.2853
5.8000	9.2640	9.2667
6.0000	9.2480	9.2466
6.5000	9.2000	9.2000
7.0000	9.1520	9.1547
7.5000	9.1120	9.1093
8.0000	9.0640	9.0653
8.5000	9.0200	9.0227
9.0000	8.9840	8.9853
9.5000	8.9520	8.9520

TIME	RATE	M*(CA*CO3-KSP/FD2)	CACO3(S)	PH	FUNTO	FUNT
0.4000	0.6083E-04	0.3191E-04	6.32	9.76	0.3080E-04	0.6262E-06
0.5000	0.5667E-04	0.3206E-04	7.48	9.76	0.3080E-04	0.6261E-06
0.6000	0.5417E-04	0.3218E-04	8.64	9.75	0.3080E-04	0.6257E-06
0.7000	0.5583E-04	0.3229E-04	9.79	9.75	0.3080E-04	0.6249E-06
0.8000	0.5917E-04	0.3239E-04	11.17	9.74	0.3080E-04	0.6240E-06
0.9000	0.6167E-04	0.3246E-04	12.55	9.73	0.3080E-04	0.6226E-06
1.0000	0.6167E-04	0.3251E-04	14.15	9.72	0.3080E-04	0.6208E-06
1.1000	0.6083E-04	0.3253E-04	15.52	9.72	0.3080E-04	0.6183E-06
1.2000	0.6083E-04	0.3251E-04	16.88	9.71	0.3080E-04	0.6154E-06
1.3000	0.6167E-04	0.3249E-04	18.01	9.70	0.3080E-04	0.6123E-06
1.4000	0.6333E-04	0.3242E-04	19.59	9.70	0.3080E-04	0.6083E-06
1.5000	0.6500E-04	0.3232E-04	21.17	9.69	0.3080E-04	0.6037E-06
1.6000	0.6750E-04	0.3221E-04	22.52	9.68	0.3080E-04	0.5991E-06
1.7000	0.7000E-04	0.3207E-04	23.87	9.67	0.3080E-04	0.5940E-06
1.8000	0.7250E-04	0.3185E-04	25.65	9.66	0.3080E-04	0.5873E-06
1.9000	0.7250E-04	0.3160E-04	27.44	9.65	0.3080E-04	0.5802E-06
2.0000	0.7000E-04	0.3134E-04	28.99	9.64	0.3080E-04	0.5730E-06
2.1000	0.6583E-04	0.3106E-04	30.53	9.63	0.3080E-04	0.5653E-06
2.2000	0.6333E-04	0.3079E-04	31.86	9.62	0.3080E-04	0.5581E-06
2.3000	0.6250E-04	0.3049E-04	33.18	9.61	0.3080E-04	0.5505E-06
2.4000	0.6250E-04	0.3018E-04	34.49	9.61	0.3080E-04	0.5425E-06
2.5000	0.6250E-04	0.2979E-04	36.02	9.59	0.3080E-04	0.5334E-06
2.6000	0.6167E-04	0.2944E-04	37.32	9.59	0.3080E-04	0.5248E-06
2.7000	0.6083E-04	0.2907E-04	38.62	9.58	0.3080E-04	0.5161E-06
2.8000	0.5867E-04	0.2868E-04	39.92	9.57	0.3080E-04	0.5070E-06
2.9000	0.5644E-04	0.2826E-04	41.22	9.56	0.3080E-04	0.4977E-06
3.0000	0.5407E-04	0.2783E-04	42.51	9.55	0.3080E-04	0.4881E-06
3.2000	0.5159E-04	0.2707E-04	44.65	9.53	0.3080E-04	0.4729E-06
3.4000	0.5006E-04	0.2627E-04	46.78	9.51	0.3080E-04	0.4570E-06
3.6000	0.4917E-04	0.2542E-04	48.90	9.49	0.3080E-04	0.4404E-06
3.8000	0.4792E-04	0.2452E-04	51.01	9.47	0.3080E-04	0.4232E-06
4.0000	0.4667E-04	0.2367E-04	52.90	9.45	0.3080E-04	0.4069E-06
4.2000	0.4500E-04	0.2271E-04	54.98	9.43	0.3080E-04	0.3888E-06
4.4000	0.4333E-04	0.2189E-04	56.65	9.41	0.3080E-04	0.3733E-06

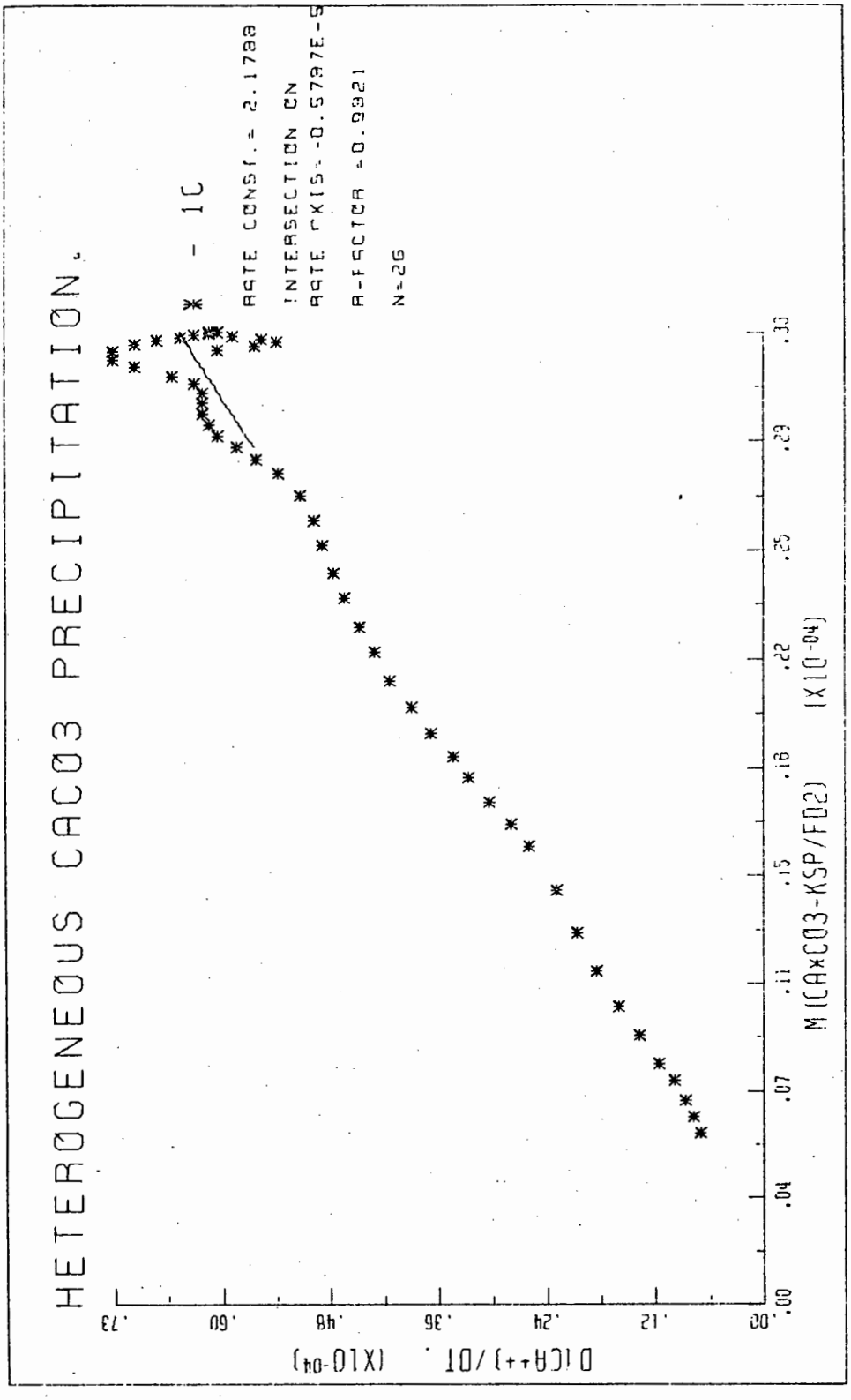
TEMPERATURE = 24.7 DEGREES CELCIUS

RATE CONSTANT = 2.1788 STANDARD DEVIATION = 0.4174

INTERSECTION ON RATE AXIS = -.5787E-05 STANDARD DEVIATION = 0.1070E-04

R-FACTOR = 0.9821

T-FACTOR = 36.9101
RATE CONSTANT(25 C) = 2.2128


HETEROGENEOUS CACO3 PRECIPITATION.
- 1C
RATE CONST.= 2.1788
INTERSECTION ON
RATE AXIS=-0.5797E-5
R-FACTOR =0.9921
N=26
D[CA++]/DT (X10-04)
M(CA*CO3-KSP/FD2) (X10-04)
.00
.04
.07
.11
.15
.18
.22
.25
.29
.33
.00
.12
.24
.36
.48
.60
.73

APPENDIX 10

PROGRAMME SOLDIV *

Programme SOLDIV numerically integrates the rate equation for calcium carbonate precipitation, i.e.

$$\frac{d[Ca^{+2}]}{dt} = K \cdot M \cdot \left([Ca^{+2}] \cdot [CO_3^{-2}] - \frac{K_{sp}}{f_D^2} \right) \qquad \ldots (A10.1)$$

It calculates all the species as a function of time during calcium carbonate precipitation. It takes the formation of ion pairs into consideration.

Calculation of Equilibrium Constants

The equilibrium constants, K_1, K_2, K_w, K_{sp}, $K_{CaCO_3^o}$ and $K_{CaHCO_3^+}$ are calculated as described in Appendix A9 (p A9.1)

Calculation of Species Concentrations at Ionic Equilibrium, when no $CaCO_3$ has as yet Precipitated

Calculation of all the species at ionic equilibrium is made as explained in Appendix A9 (p A9.2). The initial rate of $(d[Ca^{+2}])/dt$ is calculated using equation (A10.1)

Calculation of Sets of Corresponding pH, Species Concentrations and Rate

Calculation of sets of corresponding pH and species concentrations is made as explained in Appendix A9 (p A9.3). Corresponding rates of precipitation are calculated using equation (A10.1).

Calculation of Time (N) Corresponding to Calcium Concentration (N)

The rate of Ca^{+2} removal from solution may be written as follows:

$$R = \frac{d[Ca^{+2}]}{dt} = \frac{\Delta[Ca^{+2}]}{\Delta t}$$

---

*See Chapter 3, p. 143

if the increment $\Delta[Ca^{+2}]$ and Δt are small. This equation can be expanded as follows:

$$R = \frac{\Delta[Ca^{+2}]}{\Delta t}$$

$$R(N + \tfrac{1}{2}) = \frac{Ca(N) - Ca(N - 1)}{T(N) - T(N - 1)}$$

$$\therefore \quad T(N) - T(N - 1) = \left[1/R(N+\tfrac{1}{2})\right] \cdot \left[Ca(N) - Ca(N - 1)\right]$$

$$\therefore \quad T(N) = T(N - 1) + \left[1/R(N+\tfrac{1}{2})\right] \cdot \left[Ca(N) - Ca(N - 1)\right] \qquad \ldots (A10.3)$$

Hence, if T(N - 1), R(N), Ca(N) and Ca(N - 1) are known, T(N) may be calculated. Since these variables are known for T(0), the value of T(1) for a specific ΔCa can be calculated. Similarly T(2) can be calculated from values found in the calculation for T(1). The increments in ΔCa are chosen as 0,1 mg/l (as $CaCO_3$) (or $0{,}1 * 10^{-5}$ moles. l^{-1}). The calculation sequence is repeated until R(N) changes sign, i.e. dissolution of Ca^{+2} would theoretically take place.

Create a Desired Time Array for Program Output Values

A desired time array for program output values is created. The species concentrations, pH, rate and time corresponding to this new time array are selected from the table created previously and are printed as output.

Testing of Program SOLDIV

Program SOLDIV was tested as follows:

The program was supplied with reactant concentrations, temperature, crystal seed concentration and a rate constant. From the output data a plot of the rate versus $M * ([Ca^{+2}][CO_3^{-2}] - K_{sp}/f_D^2)$ was made. It was linear and the slope of the line gave a rate constant which agreed to within 1% of the input value for K.

```
C*********************************************************************
C      PROGRAM     SOLDIV
C*********************************************************************
C      THIS PROGRAM INTEGRATES THE RATE EQUATION FOR CALCIUM CARBONATE
C      PRECIPITATION  :
C
C                  R   =   K*M*(CA*CO3 - KSP/F2)
C
C      THE PROGRAM CALCULATES ALL THE SPECIES AS A FUNCTION OF TIME
C      DURING CALCIUM CARBONATE PRECIPITATION.  IT TAKES THE
C      FORMATION OF ION PAIRS CACO3 AND CAHCO3 INTO CONSIDERATION.
C*********************************************************************
C      DATA SET
C
C      FIRST DATA CARD : IDENT   (I3).
C      IDENT IS THE EXPERIMENT IDENTIFICATION NUMBER.
C
C      SECOND DATA CARD :   NAHCO3,NAOH,CACL2.  (3E10.4).
C      NAHCO3 IS THE SODIUMBICARBONATE CONCENTRATION (MOLES/L) T=0.
C      NAOH IS THE SODIUM HYDROXIDE CONCENTRATION (MOLES/L) T=0.
C      CACL2 IS THE CALCIUM CHLORIDE CONCENTRATION (MOLES/L) T=0.
C
C      THIRD DATA CARD :   TS.   (E10.4).
C      TS IS THE TEMPERATURE IN DEGREES CELCIUS.
C
C      FORTH DATA CARD :EQPH    (F6.2)
C      EQPH= IONIC EQUILIBRIUM PH AT T=0
C
C      FIFTH DATA CARD :  CACOSI,KCACO3 (2F10.4)
C      CACOSI IS THE INITIAL SEED CRRYSTAL CONCENTRATION IN MG/L.
C      KCACO3 = RATE CONSTANT
C
C*********************************************************************
       DIMENSION    HD(100),OHD(100),CO3D(100),HCO3D(100),H2CO3D(100),
      .             CACOOD(100),CAHCOD(100),UD(100),FD(100),CAD(100),
      .             CACOST(100),R(100),CACOSF(100),CCO3D(100),PHD(100),
      .             T(100),TC(100),FUNCTD(100),Y(100),Z(100),W(100)
       REAL   NA,NAHCO3,NAOH,K1,K2,KW,KCO3O,KHCO3,KCACO3,KSP
       COMMON/MIPLOT/ A,B,RR,NDIM
       N=1
       M=3
       READ(N,234)  IDENT
234    FORMAT(I3)
       WRITE(M,235)   IDENT
235    FORMAT(1H1,'EXPERIMENT  NO.',I3,///)
       READ(N,1)    NAHCO3,NAOH,CACL2
1      FORMAT(3E10.4)
       WRITE(M,2)   NAHCO3,NAOH,CACL2
2      FORMAT(1H ,'NAHCO3 = ',E10.4,4X,'NAOH = ',E10.4,4X,
      1'CACL2 = ',E10.4,///)
       NA=NAHCO3+NAOH
       CT=NAHCO3
       CAT=CACL2
       CL=2.*CACL2
       READ(N,3)    TS
3      FORMAT(E10.4)
       WRITE(M,4)   TS
4      FORMAT(1H ,'TEMPERATURE = ',E10.4,'DEGREES CELCIUS',///)
C*********************************************************************
C      CALCULATION OF EQUILIBRIUM CONSTANTS.
C*********************************************************************
       TA=TS+273.
       PK1=(17052./TA)+215.21*ALOG(TA)/ALOG(10.)-(.12675*TA)-545.56
       K1=1./10.**PK1
       PK2=(2902.39/TA)+(.02379*TA)-6.498
       K2=1./10.**PK2
       PKW=(4787.3/TA)+(7.1321*ALOG(TA)/ALOG(10.))+(.01037*TA)-22.801
       KW=1./10.**PKW
       PKSPX=0.01183*TS+8.03
       KSP=1./10.**PKSPX
       KCO3O=0.000631
       KHCO3=0.055
       WRITE(M,5)   K1,K2,KW,KHCO3,KSP,KCO3O
5      FORMAT(1H ,'K1 = ',E10.4,4X,'K2 = ',E10.4,4X,'KW = ',E10.4,
      14X,'KCAHCO3+ = ',E10.4,4X,'KSP =',E10.4,4X,'KCACO3O = ',E10.4,
      2///)
```

```
C*********************************************************************
C     CALCULATION OF SPECIES CONCETRATION AT IONIC
C     EQUILIBRIUM, T=0 ,WHEN NO CACO3 HAS AS YET PRECIPITATED.
C*********************************************************************
      READ(N,833)    EQPH
833   FORMAT(F6.2)
      WRITE(M,834)   EQPH
834   FORMAT(1H ,'EQPH = ',F6.2,//)
212   QQQQ=0.
506   RUN10=1.
      RUN11=1.
      PH=EQPH+QQQQ
      H2CO3=0.
      FMXX=0.912
      FDXX=0.692
      AH=-PH-ALOG10(FMXX)
      AH=-AH
      H=1./10.**AH
      HCO3=0.0017
307   CA=CAT/(1.+(HCO3*FDXX/KHCO3)+(K2*FDXX*HCO3/(KCO30*H)))
      CO3=CA+CT-HCO3-H2CO3-CAT
      IF(CO3-0.0)    350,350,351
350   ZZZZ=HCO3
      HCO3=ZZZZ-0.0001
      GO TO 307
351   CONTINUE
      H2CO3=H*HCO3*(FMXX**2.)/K1
      CAHCO3=CA*HCO3*FDXX/KHCO3
      CACO30=CA*CO3*(FDXX**2.)/KCO30
      OH=KW/(H*(FMXX**2.))
      CHCO3=NA+2.*CA+H+CAHCO3-CL-OH-2.*CO3
      U=0.5*(NA+H+4.*CA+CAHCO3+CL+OH+HCO3+4.*CO3)
      F=((SQRT(U)/(1.+SQRT(U)))-0.3*U)
      AFMXX=0.5*F
      FMXX=1./10.**AFMXX
      AFDXX=2.*F
      FDXX=1./10.**AFDXX
      RUN101=2.
      IF(RUN10-RUN101)    300,300,305
300   IF(HCO3-CHCO3)    303,304,305
303   Q1=0.01*HCO3
      ZHCO3=HCO3
      HCO3=ZHCO3-Q1
      GO TO 307
305   RUN10=3.
      RUN111=2.
      IF(RUN11-RUN111)   308,308,309
308   Q2=HCO3-CHCO3
      RUN11=3.
309   IF(HCO3-CHCO3)    403,311,405
405   HCO3PO=HCO3
403   Q6=0.1*Q2
      Q7=HCO3+Q6
      Q8=0.0001*HCO3
      IF(Q6-Q8)    311,311,325
325   IF(HCO3-CHCO3)   406,311,408
408   HCO3=Q7
      GO TO 307
406   HCO3=HCO3PO+0.01*Q2
      ZQ2=Q2
      Q2=0.01*ZQ2
      GO TO 307
304   CONTINUE
311   CONTINUE
      H=K2*HCO3/(CO3*FDXX)
      CPH=-ALOG10(H)+0.5*F
      QQQ=PH-CPH
      QQQA=ABS(QQQ)
      IF(QQQA-0.002)   501,501,502
502   IF(PH-CPH)   503,504,505
503   XQY=QQQQ
      QQQQ=XQY+0.001
      GO TO 506
505   YQX=QQQQ
      QQQQ=YQX-0.001
      GO TO 506
501   CONTINUE
```

```
504   CONTINUE
      HD(1)=H
      OHD(1)=OH
      CO3D(1)=CO3
      HCO3D(1)=HCO3
      H2CO3D(1)=H2CO3
      CACOOD(1)=CACO3O
      CAHCOD(1)=CAHCO3
      UD(1)=U
      FD(1)=F
      CAD(1)=CA
      PHD(1)=CPH
      WRITE(M,806)   PHD(1)
806   FORMAT(' CALCULATED EQUILIBRIUM PH = ',F6.2,//)
      READ(N,21)   CACOSI,KCACO3
21    FORMAT(2F10.4)
      WRITE(M,22)  CACOSI,KCACO3
22    FORMAT(' CACO3 SEED CRYSTAL CONC. =',F10.4,5X,'RATE CONSTAT K =',F
     .10.4,//)
      R(1)=CACOSI*KCACO3*(CA*CO3-KSP/(FDXX**2.))
      CACOSF(1)=0.0
C*********************************************************************
C     CREATE A TABLE WITH PH- AND CORRESPONDING SPECIES
C     CONCENTRATIONS VALUES.
C*********************************************************************
      DO   23   N=2,100
      NN=N-1
      H=0.000005
      CAD(N)=CAD(NN)-H
      CO3D(N)=CO3D(NN)-H
      H2CO3D(N)=H2CO3D(NN)
      FD(N)=FD(NN)
      RUN3=1.
      RUN4=1.
      AA4=CAD(N)
      CCCC=0.0
      NT=1
995   XXXZ=CO3D(N)+CCCC
28    AA3=CO3D(N)
      IF(NT.EQ.1) GO TO 888
      HCO3D(N)=H2CO3D(1)+HCO3D(1)+CO3D(1)-H2CO3D(N)-CO3D(N)-CAD(1)
     1+CAD(N)
      NT=2
      GO TO 889
888   HCO3D(N)=HCO3D(NN)
889   CONTINUE
      AA2=HCO3D(N)
      AH=ALOG10(K2)-ALOG10(AA3)+ALOG10(AA2)+2.*FD(N)
      AH=-AH
      HD(N)=1./10.**AH
      AA7=HD(N)
      AH2CO3=ALOG10(AA7)+ALOG10(AA2)-ALOG10(K1)-FD(N)
      AH2CO3=-AH2CO3
      H2CO3D(N)=1./10.**AH2CO3
      AA1=H2CO3D(N)
      AOH=ALOG10(KW)-ALOG10(AA7)+FD(N)
      AOH=-AOH
      OHD(N)=1./10.**AOH
      AA8=OHD(N)
      PHD(N)=-ALOG10(AA7)+0.5*FD(N)
      ACACOO=ALOG10(AA4)+ALOG10(AA3)-ALOG10(KCO3O)-4.*FD(N)
      ACACOO=-ACACOO
      CACOOD(N)=1./10.**ACACOO
      AA5=CACOOD(N)
      ACAHCO=ALOG10(AA4)+ALOG10(AA2)-ALOG10(KHCO3)-2.*FD(N)
      ACAHCO=-ACAHCO
      CAHCOD(N)=1./10.**ACAHCO
      AA6=CAHCOD(N)
      U=0.5*(CAHCOD(N)+NA+HD(N)+4.*CAD(N)+CL+OHD(N)+HCO3D(N)
     1+4.*CO3D(N))
      FD(N)=(SQRT(U)/(1.+SQRT(U)))-0.3*U
      CCO3D(N)=.5*(CAHCOD(N)+NA+HD(N)+2.*CAD(N)-CL-OHD(N)-HCO3D(N))
      IF(CCO3D(N)-0.0)     900,900,901
901   CONTINUE
      CO3D(N)=XXXZ
      CCC=CO3D(N)-CCO3D(N)
      CCCA=ABS(CCC)
```

```
      IF(CCCA-0.0000002)      990,990,991
991   IF(CO3D(N)-CCO3D(N))     992,993,994
992   ZXQY=CCCC
      CCCC=ZXQY+0.0000001
      GO TO  995
994   ZXYQ=CCCC
      CCCC=ZXYQ-0.0000001
      GO TO 995
990   CONTINUE
993   CONTINUE
      CAT0=CAD(1)+CAHCOD(1)+CACOOD(1)
      CATN=CAD(N)+CAHCOD(N)+CACOOD(N)
      CACOSF(N)=CAT0-CATN
      CACOSF(N)=100000.*CACOSF(N)
      CACOST(N)=CACOSI+CACOSF(N)
      AF2=2.*FD(N)
      F2=(1./10.**AF2)**2.
      PKSF2=KSP/F2
      R(N)=CACOST(N)*KCACO3*(CAD(N)*CO3D(N)-PKSF2)
      IF(R(N)-0.0)  996,996,997
997   CONTINUE
23    CONTINUE
900   CONTINUE
216   CONTINUE
      N=100
996   CONTINUE
      N=N-1
      WRITE(M,813)   N
813   FORMAT(' N=',I3,//)
C*************************************************************************
C     INTEGRATION ROUTINE.
C*************************************************************************
      WRITE(M,816)
816   FORMAT('1CA++          PH          R(N)          1./R(N)',//)
      DO 701 K=1,N
      Y(K)=1./R(K)
      W(K)=R(K)/KCACO3
      WRITE(M,817) CAD(K),PHD(K),R(K),Y(K)
817   FORMAT(4(E10.4,3X))
701   CONTINUE
      CALL QSF(H,Y,Z,N)
      WRITE(M,815)
815   FORMAT('1      TIME          CA++          PH          CACO30
     *         CACO3(PREC)     M*(CA*CO3-KSP/FD2)',//)
      WRITE(M,812) (Z(I),CAD(I),PHD(I),CACOOD(I),CACOSF(I),W(I),I=1,N)
812   FORMAT(6(5X,E10.4))
      RETURN
      END
```

EXPERIMENT NO. 35

NAHCO3 = 0.1563E-02 NAOH = 0.6874E-03 CACL2 = 0.9648E-03

TEMPERATURE = 0.2472E 02DEGREES CELCIUS

K1 = 0.4291E-06 K2 = 0.4640E-10 KW = 0.9781E-14 KCAHCO3+ = 0.5500E-01 KSP =0.4760E-08

KCACO3O = 0.6310E-03

EQPH = 9.85

CALCULATED EQUILIBRIUM PH = 9.84

CACO3 SEED CRYSTAL CONC. = 900.0000 RATE CONSTAT K = 2.0730

N= 78

CA++	PH	R(N)	1./R(N)
.7187E-03	0.9845E 01	0.4921E-03	0.2032E 04
.7137E-03	0.9839E 01	0.4820E-03	0.2075E 04
.7087E-03	0.9833E 01	0.4729E-03	0.2115E 04
.7037E-03	0.9828E 01	0.4641E-03	0.2155E 04
.6987E-03	0.9823E 01	0.4550E-03	0.2198E 04
.6937E-03	0.9817E 01	0.4460E-03	0.2242E 04
.6887E-03	0.9812E 01	0.4375E-03	0.2286E 04
.6937E-03	0.9806E 01	0.4286E-03	0.2333E 04
.6787E-03	0.9801E 01	0.4199E-03	0.2382E 04
.6737E-03	0.9795E 01	0.4114E-03	0.2430E 04
.6687E-03	0.9789E 01	0.4028E-03	0.2483E 04
.6637E-03	0.9783E 01	0.3942E-03	0.2537E 04
.6587E-03	0.9777E 01	0.3860E-03	0.2591E 04
.6537E-03	0.9771E 01	0.3775E-03	0.2649E 04
.6487E-03	0.9765E 01	0.3695E-03	0.2706E 04
.6437E-03	0.9759E 01	0.3612E-03	0.2769E 04
.6387E-03	0.9753E 01	0.3529E-03	0.2833E 04
.6337E-03	0.9746E 01	0.3451E-03	0.2898E 04

TIME	CA++	PH	CACO3D	CACO3(PREC)	M*(CA*CO3-KSP/FD2)
0.0	0.7187E-03	0.9845E 01	0.2408E-03	0.0	0.2374E-03
0.1027E-01	0.7137E-03	0.9839E 01	0.2362E-03	0.9706E 00	0.2325E-03
0.2074E-01	0.7087E-03	0.9833E 01	0.2316E-03	0.1935E 01	0.2281E-03
0.3141E-01	0.7037E-03	0.9828E 01	0.2274E-03	0.2860E 01	0.2239E-03
0.4229E-01	0.6987E-03	0.9823E 01	0.2232E-03	0.3788E 01	0.2195E-03
0.5339E-01	0.6937E-03	0.9817E 01	0.2189E-03	0.4719E 01	0.2152E-03
0.6471E-01	0.6887E-03	0.9812E 01	0.2148E-03	0.5635E 01	0.2110E-03
0.7626E-01	0.6837E-03	0.9806E 01	0.2107E-03	0.6554E 01	0.2068E-03
0.8805E-01	0.6787E-03	0.9801E 01	0.2066E-03	0.7475E 01	0.2025E-03
0.1001E 00	0.6737E-03	0.9795E 01	0.2026E-03	0.8381E 01	0.1985E-03
0.1124E 00	0.6687E-03	0.9789E 01	0.1985E-03	0.9290E 01	0.1943E-03
0.1249E 00	0.6637E-03	0.9783E 01	0.1945E-03	0.1020E 02	0.1901E-03
0.1377E 00	0.6587E-03	0.9777E 01	0.1906E-03	0.1110E 02	0.1862E-03
0.1508E 00	0.6537E-03	0.9771E 01	0.1866E-03	0.1200E 02	0.1821E-03
0.1642E 00	0.6487E-03	0.9765E 01	0.1828E-03	0.1289E 02	0.1783E-03
0.1779E 00	0.6437E-03	0.9759E 01	0.1789E-03	0.1378E 02	0.1742E-03
0.1919E 00	0.6387E-03	0.9753E 01	0.1750E-03	0.1468E 02	0.1703E-03
0.2062E 00	0.6337E-03	0.9746E 01	0.1713E-03	0.1556E 02	0.1665E-03
0.2209E 00	0.6287E-03	0.9740E 01	0.1675E-03	0.1644E 02	0.1626E-03
0.2359E 00	0.6237E-03	0.9733E 01	0.1637E-03	0.1732E 02	0.1587E-03
0.2513E 00	0.6187E-03	0.9726E 01	0.1601E-03	0.1819E 02	0.1550E-03
0.2670E 00	0.6137E-03	0.9720E 01	0.1564E-03	0.1907E 02	0.1512E-03
0.2832E 00	0.6087E-03	0.9712E 01	0.1527E-03	0.1994E 02	0.1474E-03
0.2998E 00	0.6037E-03	0.9705E 01	0.1492E-03	0.2080E 02	0.1439E-03
0.3167E 00	0.5987E-03	0.9698E 01	0.1456E-03	0.2167E 02	0.1401E-03
0.3342E 00	0.5937E-03	0.9691E 01	0.1421E-03	0.2252E 02	0.1366E-03
0.3521E 00	0.5887E-03	0.9684E 01	0.1386E-03	0.2338E 02	0.1330E-03
0.3704E 00	0.5837E-03	0.9676E 01	0.1351E-03	0.2423E 02	0.1294E-03
0.3893E 00	0.5787E-03	0.9668E 01	0.1317E-03	0.2508E 02	0.1260E-03
0.4087E 00	0.5737E-03	0.9660E 01	0.1283E-03	0.2592E 02	0.1225E-03
0.4287E 00	0.5687E-03	0.9652E 01	0.1249E-03	0.2677E 02	0.1190E-03
0.4493E 00	0.5637E-03	0.9644E 01	0.1216E-03	0.2760E 02	0.1157E-03
0.4705E 00	0.5587E-03	0.9636E 01	0.1184E-03	0.2844E 02	0.1123E-03
0.4923E 00	0.5537E-03	0.9627E 01	0.1151E-03	0.2927E 02	0.1090E-03
0.5147E 00	0.5487E-03	0.9619E 01	0.1119E-03	0.3010E 02	0.1057E-03

APPENDIX 11

RAW DATA FOR EXPERIMENTS ON CONTINUOUS LIME TREATMENT OF SECONDARY EFFLUENT IN CSTR SYSTEMS - LABORATORY STUDIES*

Raw data collected during the investigation of continuous lime treatment of secondary effluent in laboratory CSTR systems are listed below. The following codes are used,

HTE + LIME TO PH X - Lime addition to control pH X
NA - Total dissolved sodium (mg ℓ^{-1} as Na)
K - Total dissolved potassium (mg ℓ^{-1} as K)
CL - Total dissolved chlorides (mg ℓ^{-1} as Cl)
SO_4 - Total dissolved sulphates (mg ℓ^{-1} as SO_4)
NO_3 - Total dissolved nitrates (mg ℓ^{-1} as N)
NO_2 - Total dissolved nitrites (mg ℓ^{-1} as N)
ORG-C-Total dissolved organic carbon (mg ℓ^{-1} as C)
TOT.P - Total dissolved phosphorus (mg ℓ^{-1} as P)
TKN - Total dissolved organic nitrogen (mg ℓ^{-1} as N)
RN - Reactor identification code
ID - Sample identification code
HRT - Hydraulic retention time (min)**
MRT - Mean residence time (min)**
PHR - Reactor effluent pH
PHF - pH of filtered reactor effluent
ALK - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)
CAF - Residual total dissolved calcium (mg ℓ^{-1} as Ca)
CAT - Total calcium (mg ℓ^{-1} as Ca)

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*See Chapter 4, p. 176 and Chapter 6, p. 290

**Retention times longer than 16,0 minutes are in fact batch reaction times indicated in *hour* units.

MGF - Total magnesium (mg ℓ^{-1} as Mg)

THF - Total dissolved hardness (mg ℓ^{-1} as $CaCO_3$)

PO_4 - Total dissolved ortho-phosphate (mg ℓ^{-1} as P)

COD - Total dissolved chemical oxygen demand (mg ℓ^{-1} as O)

NH_3 - Total dissolved free and saline ammonia (mg ℓ^{-1} as N)

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EXPERIMENT NO.= 6.

HTE+LIME TO PH=11.2

NA= 48. K= 10. CL= 55. SO4= 38. NO3= 7.5 NO2= 1.5 ORG-C= 19. TOT.P= 7.2 TKN=

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	6.00	******	******	*****	7.74	200.0	49.0	50.0	20.5	20.4	190.0	6.0	60.	8.1
2.	6.08	0.98	1.07	11.22	11.40	314.0	108.0	248.0	10.7	22.5	330.0	0.0	*****	6.7
2.	6.07	0.98	1.07	11.21	11.38	308.0	105.0	258.0	10.8	23.0	350.0	0.0	*****	6.9
2.	6.06	1.30	1.40	11.23	11.52	270.0	100.0	250.0	5.7	23.0	280.0	0.0	*****	6.4
2.	6.05	1.30	1.40	11.21	11.28	292.0	98.0	242.0	12.6	23.0	300.0	0.0	*****	6.7
2.	6.04	1.95	1.85	11.23	11.20	274.0	86.0	212.0	12.8	22.0	280.0	0.0	*****	7.0
2.	6.03	1.95	1.85	11.22	11.23	272.0	85.0	220.0	12.5	22.5	280.0	0.0	*****	7.0
2.	6.02	3.91	3.42	11.21	11.10	232.0	73.0	198.0	13.4	21.5	231.0	0.0	*****	7.0
2.	6.01	3.91	3.42	11.20	11.20	234.0	74.0	216.0	13.6	22.0	272.0	0.0	*****	7.0
1.	6.16	3.84	3.56	11.21	11.13	244.0	74.0	206.0	14.0	22.0	224.0	0.0	24.	6.4
1.	6.15	3.84	3.56	11.21	11.18	264.0	71.0	194.0	14.5	22.0	250.0	0.0	20.	6.5
1.	6.14	5.13	5.17	11.22	11.20	238.0	65.0	200.0	14.0	22.0	217.0	0.0	19.	6.7
1.	6.13	5.13	5.17	11.22	11.18	240.0	67.0	202.0	14.2	22.4	210.0	0.0	20.	6.7
1.	6.12	7.69	7.45	11.22	11.12	222.0	63.0	194.0	13.7	22.0	223.0	0.0	24.	6.4
1.	6.11	7.69	7.45	11.22	11.11	216.0	58.0	188.0	12.7	22.0	214.0	0.0	22.	6.1
1.	6.10	15.38	14.00	11.20	11.10	199.0	54.0	186.0	12.3	21.6	174.0	0.0	20.	6.2
1.	6.09	15.38	14.00	11.19	11.10	187.0	53.0	202.0	12.2	22.0	190.0	0.0	23.	6.7
1.	6.17	72.00	******	*****	11.10	122.0	37.0	*****	0.5	*****	*****	0.0	24.	5.2
1.	6.18	72.00	******	*****	11.09	98.0	30.0	*****	0.4	*****	*****	0.0	24.	5.3
2.	6.19	96.00	******	*****	11.67	211.0	63.0	*****	0.1	*****	*****	0.0	28.	5.5
2.	6.20	96.00	******	*****	11.69	211.0	55.0	*****	0.1	*****	*****	0.0	29.	5.8
1.	6.21	240.00	******	*****	10.71	112.0	21.0	*****	0.3	*****	*****	0.0	30.	4.5
1.	6.22	240.00	******	*****	10.60	85.0	18.0	*****	0.1	*****	*****	0.0	28.	4.6
2.	6.23	240.00	******	*****	11.41	202.0	48.0	*****	0.1	*****	*****	0.0	29.	4.6
2.	6.24	240.00	******	*****	11.48	200.0	51.0	*****	0.2	*****	*****	0.0	33.	4.9

EXPERIMENT NO.= 7.

HTE+LIME TO PH 11.4

NA= 48. K= 13. CL= 46. SO4= 44. NO3= 7.0 NO2= 1.0 ORG-C= 14. TOT.P= 8.8 TKN=

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	7.00	******	******	*****	7.80	195.0	43.0	44.0	19.8	20.0	216.0	8.7	35.	10.9
2.	7.08	0.98	1.07	11.41	11.70	362.0	130.0	308.0	5.5	22.0	365.0	0.0	24.	8.4
2.	7.07	0.98	1.07	11.41	11.68	353.0	126.0	308.0	6.3	21.8	350.0	0.0	23.	8.8
2.	7.06	1.30	1.40	11.42	11.70	338.0	116.0	291.0	5.4	21.7	345.0	0.0	25.	8.4
2.	7.05	1.30	1.40	11.41	11.60	340.0	116.0	287.0	5.8	21.3	325.0	0.0	21.	8.8
2.	7.04	1.95	1.85	11.42	11.50	295.0	98.0	242.0	7.2	21.2	260.0	0.0	21.	8.8
2.	7.03	1.95	1.85	11.40	11.43	291.0	91.0	249.0	7.7	21.0	285.0	0.0	29.	9.0
2.	7.02	3.91	3.42	11.41	11.41	258.0	81.0	217.0	7.5	20.7	260.0	0.0	25.	8.8
2.	7.01	3.91	3.42	11.42	11.43	266.0	81.0	224.0	7.5	20.8	250.0	0.0	24.	8.8
1.	7.16	3.84	3.56	11.42	11.40	253.0	88.0	221.0	7.8	20.8	260.0	0.0	22.	8.3
1.	7.15	3.84	3.56	11.42	11.40	253.0	84.0	228.0	7.7	20.9	260.0	0.0	21.	8.0
1.	7.14	5.13	5.17	11.41	11.39	243.0	81.0	217.0	7.8	21.0	250.0	0.0	23.	8.1
1.	7.13	5.13	5.17	11.43	11.42	247.0	84.0	217.0	7.5	20.8	235.0	0.0	19.	8.3
1.	7.12	7.69	7.45	11.42	11.40	231.0	77.0	207.0	7.3	20.8	235.0	0.0	21.	8.3
1.	7.11	7.69	7.45	11.42	11.38	235.0	74.0	214.0	7.3	20.5	240.0	0.0	24.	8.7
1.	7.10	15.38	14.00	11.40	11.34	204.0	70.0	203.0	6.2	20.5	215.0	0.0	21.	8.4
1.	7.09	15.38	14.00	11.41	11.38	211.0	70.0	214.0	5.6	20.5	215.0	0.0	20.	8.5
1.	7.17	24.00	******	*****	11.41	162.0	49.0	*****	*****	*****	*****	0.0	24.	6.3
1.	7.18	24.00	******	*****	11.42	145.0	44.0	*****	*****	*****	*****	0.0	25.	6.7
2.	7.19	24.00	******	*****	11.89	313.0	99.0	*****	*****	*****	*****	0.0	25.	6.8
2.	7.20	24.00	******	*****	11.92	311.0	84.0	*****	*****	*****	*****	0.0	26.	6.4
1.	7.21	192.00	******	*****	11.11	141.0	35.0	*****	0.3	*****	*****	0.0	39.	6.0
1.	7.22	192.00	******	*****	11.11	132.0	32.0	*****	0.1	*****	*****	0.0	27.	6.6
2.	7.23	192.00	******	*****	11.71	280.0	65.0	*****	0.1	*****	*****	0.0	39.	6.1
2.	7.24	192.00	******	*****	11.78	305.0	78.0	*****	0.1	*****	*****	0.0	28.	6.6

EXPERIMENT NO.= 8.

HTE+LIME TO PH=11.0

NA= 49. K= 13. CL= 44. SO4= 42. NO3= 6.4 NO2= 0.7 ORG-C= 16. TOT.P= 8.5 TKN=

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	8.00	******	******	*****	7.78	197.0	40.0	47.0	20.0	20.0	198.0	8.0	31.	11.3
2.	8.08	0.98	1.07	10.99	11.31	301.0	92.0	247.0	13.0	22.0	262.0	0.0	28.	9.0
2.	8.07	0.98	1.07	11.04	11.33	314.0	99.0	252.0	12.0	22.0	272.0	0.0	27.	9.1
2.	8.06	1.30	1.40	11.03	11.20	298.0	88.0	223.0	14.0	22.0	282.0	0.0	27.	9.3
2.	8.05	1.30	1.40	11.03	11.28	292.0	88.0	223.0	13.0	22.0	250.0	0.0	29.	9.0
2.	8.04	1.95	1.85	11.01	11.10	273.0	76.0	216.0	15.0	21.0	242.0	0.0	29.	9.1
2.	8.03	1.95	1.85	11.01	11.12	276.0	71.0	208.0	15.0	21.0	240.0	0.0	30.	9.2
2.	8.02	3.91	3.42	11.01	11.00	249.0	64.0	188.0	15.0	21.0	224.0	0.0	29.	9.2
2.	8.01	3.91	3.42	11.00	11.00	249.0	66.0	186.0	15.0	21.0	217.0	0.0	33.	9.2
1.	8.16	3.84	3.56	11.02	10.93	249.0	66.0	193.0	16.0	21.0	217.0	0.0	25.	9.0
1.	8.15	3.84	3.56	11.01	10.89	252.0	66.0	193.0	16.0	21.0	234.0	0.0	30.	9.3
1.	8.14	5.13	5.17	11.02	10.93	240.0	62.0	186.0	16.0	21.0	224.0	0.0	40.	9.3
1.	8.13	5.13	5.17	11.01	10.90	232.0	62.0	187.0	16.0	21.0	224.0	0.0	27.	9.3
1.	8.12	7.69	7.45	11.02	10.88	230.0	58.0	183.0	16.0	21.0	200.0	0.0	25.	9.0
1.	8.11	7.69	7.45	10.99	10.89	230.0	56.0	183.0	16.0	21.0	200.0	0.0	26.	9.0
1.	8.10	15.38	14.00	11.00	10.83	207.0	48.0	177.0	15.0	21.0	187.0	0.0	24.	8.8
1.	8.09	15.38	14.00	11.01	10.82	203.0	52.0	182.0	14.0	21.0	198.0	0.0	26.	9.0
1.	8.17	24.00	******	*****	10.80	118.0	34.0	*****	1.9	*****	*****	0.0	26.	6.9
1.	8.18	24.00	******	*****	10.90	106.0	27.0	*****	3.7	*****	*****	0.0	29.	6.4
2.	8.19	24.00	******	*****	11.53	205.0	52.0	*****	0.7	*****	*****	0.0	27.	6.8
2.	8.20	24.00	******	*****	11.57	187.0	57.0	*****	0.2	*****	*****	0.0	31.	7.0
1.	8.21	134.00	******	*****	10.53	112.0	23.0	*****	0.7	*****	*****	0.0	27.	7.2
1.	8.22	134.00	******	*****	10.41	89.0	28.0	*****	0.5	*****	*****	0.0	25.	7.0
2.	8.23	134.00	******	*****	11.39	174.0	41.0	*****	0.3	*****	*****	0.0	25.	6.8
2.	8.24	134.00	******	*****	11.38	173.0	42.0	*****	0.1	*****	*****	0.0	30.	7.0

EXPERIMENT NO.= 9.

HTE+LIME TO PH=10.5

NA= 48. K= 12. CL= 47. SO4= 42. NO3= 3.8 NO2= 0.5 ORG-C= 18. TOT.P= 6.9 TKN=

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	9.00	******	******	*****	7.78	199.0	42.0	42.0	19.0	19.3	173.0	6.8	28.	12.0
2.	9.08	0.98	1.07	10.54	11.08	287.0	77.0	222.0	13.5	20.9	250.0	0.0	25.	9.6
2.	9.07	0.98	1.07	10.53	11.08	291.0	80.0	212.0	13.3	20.8	240.0	0.0	26.	9.2
2.	9.06	1.30	1.40	10.51	10.80	268.0	76.0	196.0	15.4	20.5	230.0	0.0	27.	10.0
2.	9.05	1.30	1.40	10.53	10.89	282.0	77.0	200.0	16.0	20.6	240.0	0.0	31.	10.1
2.	9.04	1.95	1.85	10.53	10.74	258.0	65.0	180.0	16.3	20.4	214.0	0.0	25.	10.0
2.	9.03	1.95	1.85	10.53	10.72	261.0	64.0	182.0	16.7	20.4	217.0	0.0	26.	9.9
2.	9.02	3.91	3.42	10.54	10.56	239.0	56.0	165.0	16.7	20.2	200.0	0.0	27.	10.1
2.	9.01	3.91	3.42	10.57	10.58	243.0	56.0	157.0	16.7	20.0	200.0	0.0	25.	10.0
1.	9.16	3.84	3.56	10.51	10.51	248.0	59.0	175.0	16.7	20.2	224.0	0.0	28.	9.3
1.	9.15	3.84	3.56	10.50	10.50	249.0	61.0	165.0	17.2	20.6	215.0	0.0	29.	9.2
1.	9.14	5.13	5.17	10.50	10.41	242.0	56.0	166.0	16.8	20.3	216.0	0.0	30.	9.1
1.	9.13	5.13	5.17	10.51	10.42	243.0	58.0	166.0	17.0	20.2	210.0	0.0	27.	9.6
1.	0.91	7.69	7.45	10.52	10.39	234.0	54.0	163.0	17.1	20.3	198.0	0.0	19.	9.2
1.	9.11	7.69	7.45	10.51	10.41	236.0	53.0	159.0	17.0	20.3	207.0	0.0	28.	9.9
1.	9.10	15.38	14.00	10.50	10.35	223.0	50.0	158.0	17.0	20.0	190.0	0.0	30.	9.9
1.	9.09	15.38	14.00	10.50	10.32	214.0	54.0	158.0	16.8	20.3	210.0	0.0	27.	9.7
1.	9.17	48.00	******	*****	10.31	144.0	36.0	*****	7.0	*****	*****	0.0	37.	9.2
1.	9.18	48.00	******	*****	10.32	114.0	16.0	*****	7.8	*****	*****	0.0	30.	8.5
2.	9.19	48.00	******	*****	11.13	151.0	42.0	*****	0.5	*****	*****	0.0	27.	8.1
2.	9.20	48.00	******	*****	11.07	123.0	36.0	*****	0.2	*****	*****	0.0	35.	7.7
1.	9.21	144.00	******	*****	10.20	133.0	29.0	*****	4.8	*****	145.0	0.1	30.	7.9
1.	9.22	144.00	******	*****	10.20	99.0	14.0	*****	5.5	*****	69.0	0.3	22.	8.0
2.	9.23	144.00	******	*****	11.10	138.0	26.0	*****	0.5	*****	97.0	0.0	22.	7.9
2.	9.24	144.00	******	*****	10.99	114.0	28.0	*****	0.3	*****	84.0	0.0	24.	7.4

EXPERIMENT NO.= 10.

HTE+LIME TO PH=10.0

NA= 48. K= 13. CL= 50. SO4= 41. NO3= 8.4 NO2= 0.5 ORG-C= 20. TOT.P= 7.3 TKN=

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	10.00	******	******	*****	7.90	175.0	41.0	46.0	19.6	19.0	168.0	7.2	33.	7.8
2.	10.08	0.98	1.07	10.02	10.10	252.0	60.0	130.0	18.0	20.2	260.0	0.3	26.	5.0
2.	10.07	0.98	1.07	10.02	10.09	251.0	53.0	124.0	18.2	20.7	270.0	0.2	33.	4.8
2.	10.06	1.30	1.40	10.01	10.00	240.0	56.0	130.0	18.2	20.0	235.0	0.3	35.	5.2
2.	10.05	1.30	1.40	10.03	10.08	241.0	57.0	123.0	18.2	20.5	240.0	0.2	30.	5.2
2.	10.04	1.95	1.85	9.99	9.93	234.0	55.0	116.0	18.2	20.3	240.0	0.3	34.	5.3
2.	10.03	1.95	1.85	10.03	9.98	236.0	56.0	115.0	18.5	20.3	235.0	0.3	31.	5.5
2.	10.02	3.91	3.42	9.98	9.91	217.0	52.0	114.0	18.3	20.0	225.0	0.3	32.	5.2
2.	10.01	3.91	3.42	10.03	9.92	229.0	53.0	123.0	18.3	20.3	240.0	0.3	31.	5.2
1.	10.16	3.84	3.56	10.01	9.80	238.0	46.0	106.0	18.3	20.0	220.0	0.5	23.	4.2
1.	10.15	3.84	3.56	10.00	9.81	239.0	51.0	108.0	18.9	19.7	240.0	0.5	26.	4.2
1.	10.14	5.13	5.17	10.01	9.82	236.0	50.0	106.0	18.8	20.3	240.0	0.7	26.	4.3
1.	10.13	5.13	5.17	10.00	9.82	236.0	54.0	107.0	18.5	20.4	255.0	0.6	26.	4.3
1.	10.12	7.69	7.45	10.00	9.82	232.0	58.0	104.0	18.4	19.9	220.0	0.6	25.	4.6
1.	10.11	7.69	7.45	10.04	9.86	235.0	51.0	108.0	18.4	20.0	220.0	0.4	24.	4.7
1.	10.10	15.38	14.00	9.99	9.81	229.0	50.0	102.0	18.5	19.9	240.0	0.6	27.	4.7
1.	10.09	15.38	14.00	10.04	9.97	228.0	55.0	108.0	17.8	20.5	220.0	0.4	24.	4.5
1.	10.17	96.00	******	*****	9.61	160.0	44.0	*****	18.1	*****	169.0	0.4	26.	1.9
1.	10.18	96.00	******	*****	9.20	110.0	27.0	*****	18.0	*****	124.0	2.1	27.	1.3
2.	10.19	24.00	******	*****	10.18	169.0	37.0	*****	16.2	*****	*****	0.1	32.	4.1
2.	10.20	24.00	******	*****	10.02	125.0	20.0	*****	15.8	*****	*****	0.3	30.	4.0
1.	10.21	144.00	******	*****	9.37	144.0	43.0	*****	17.2	*****	*****	*****	*****	*****
1.	10.22	144.00	******	*****	8.61	102.0	23.0	*****	17.4	*****	*****	*****	*****	*****
2.	10.23	120.00	******	*****	10.00	154.0	33.0	*****	15.2	*****	124.0	0.5	25.	3.8
2.	10.24	120.00	******	*****	9.90	114.0	29.0	*****	15.2	*****	144.0	0.2	24.	4.0

EXPERIMENT NO.= 35.

HTE+LINE TO PH=11.2

NA= 44. K= 12. CL= 38. SO4= 45. NO3= 7.5 NO2= 1.5 ORG-C= 7. TOT.P= 7.5 TKN= 5

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	35.00	******	******	*****	7.80	168.0	28.0	38.0	19.0	19.3	176.0	7.3	22.	4.3
2.	35.09	0.98	1.07	11.21	11.18	259.0	79.0	200.0	13.2	20.7	295.0	0.0	25.	3.8
2.	35.08	0.98	1.07	11.23	11.31	259.0	89.0	230.0	11.7	21.0	198.0	0.0	27.	4.0
2.	35.07	0.98	1.07	11.22	11.11	221.0	70.0	246.0	11.7	21.4	260.0	0.0	23.	3.6
2.	35.06	1.30	1.40	11.22	11.17	260.0	79.0	178.0	13.5	20.2	280.0	0.0	26.	3.8
2.	35.05	1.30	1.40	11.19	11.12	256.0	73.0	174.0	13.7	20.0	255.0	0.0	24.	3.5
2.	35.04	1.95	1.85	11.20	11.09	237.0	68.0	174.0	13.5	19.9	210.0	0.0	24.	3.4
2.	35.03	1.95	1.85	11.21	11.09	233.0	73.0	174.0	14.2	19.8	240.0	0.0	27.	3.4
2.	35.02	3.91	3.42	11.20	11.00	212.0	57.0	160.0	13.5	19.6	210.0	0.0	25.	3.4
2.	35.01	3.91	3.42	11.22	11.02	219.0	60.0	160.0	13.5	19.7	215.0	0.0	27.	4.2
1.	35.17	3.84	3.56	11.22	11.00	226.0	56.0	156.0	15.1	20.0	255.0	0.0	29.	3.4
1.	35.16	3.84	3.56	11.20	11.00	225.0	56.0	154.0	15.0	20.2	280.0	0.0	27.	3.5
1.	35.15	5.13	5.17	11.22	11.00	213.0	56.0	152.0	14.0	20.1	194.0	0.0	28.	3.7
1.	35.14	5.13	5.17	11.23	11.10	216.0	56.0	160.0	13.6	20.2	194.0	0.0	26.	3.3
1.	35.13	7.69	7.45	11.21	10.92	204.0	57.0	158.0	13.5	20.3	187.0	0.0	25.	3.5
1.	35.12	7.69	7.45	11.20	10.93	203.0	54.0	160.0	13.4	19.8	200.0	0.0	27.	3.8
1.	35.11	15.38	14.00	11.20	10.90	178.0	50.0	152.0	11.3	19.7	168.0	0.0	24.	3.4
1.	35.10	15.38	14.00	11.21	10.92	176.0	48.0	162.0	10.4	20.0	167.0	0.0	24.	3.5
1.	35.18	24.00	0.0	0.0	10.85	117.0	41.0	0.0	4.5	0.0	136,0	0.0	101.	3.5
1.	35.19	24.00	0.0	0.0	10.80	83.0	29.0	0.0	4.5	0.0	110.0	0.0	110.	4.0
2.	35.20	24.00	0.0	0.0	10.82	109.0	40.0	0.0	3.0	0.0	124.0	0.0	106.	3.4
2.	35.21	24.00	0.0	0.0	10.82	91.0	30.0	0.0	3.8	0.0	106.0	0.0	103.	3.8
1.	35.22	72.00	0.0	0.0	10.55	122.0	51.0	0.0	8.5	0.0	176.0	0.0	20.	3.3
1.	35.23	72.00	0.0	0.0	10.46	74.0	48.0	0.0	8.7	0.0	150.0	0.0	28.	3.7
2.	35.24	72.00	0.0	0.0	10.60	108.0	61.0	0.0	4.0	0.0	165.0	0.0	25.	3.0
2.	35.25	72.00	0.0	0.0	10.54	70.0	34.0	0.0	6.4	0.0	118.0	0.0	25.	3.0

EXPERIMENT NO.= 36.

EFFECT OF SLUDGE/NO SLUDGE

NA= 47. K= 13. CL= 53. SO4= 46. NO3= 7.5 NO2= 1.5 ORG-C= 4. TOT.P= 7.5 TKN= 3.

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	36.00	******	******	*****	7.65	166.0	38.0	39.0	20.0	20.8	190.0	7.4	29.	4.7
2.	36.08	1.30	0.98	11.20	10.79	136.0	37.0	*****	5.0	563.0	130.0	0.0	46.	8.0
2.	36.07	1.12	1.12	11.20	10.82	135.0	39.0	*****	4.7	544.0	133.0	0.0	42.	7.6
2.	36.06	0.98	1.07	11.22	11.03	270.0	70.0	184.0	14.5	21.2	260.0	0.0	26.	3.4
2.	36.05	0.98	1.07	11.22	11.05	261.0	69.0	204.0	13.4	24.4	240.0	0.0	25.	4.3
2.	36.04	1.95	1.64	11.20	10.80	127.0	37.0	*****	4.5	450.0	124.0	0.0	44.	7.2
2.	36.03	1.95	1.64	11.21	10.90	134.0	39.0	*****	4.7	*****	113.0	0.0	43.	7.9
2.	36.02	1.95	1.85	11.24	11.12	245.0	67.0	176.0	13.3	21.6	225.0	0.0	30.	3.8
2.	36.01	1.95	1.85	11.19	11.20	242.0	70.0	202.0	12.8	22.4	240.0	0.0	34.	4.7
1.	36.16	7.69	6.62	11.20	10.79	112.0	50.0	*****	5.3	469.0	130.0	0.0	43.	7.0
1.	36.15	7.69	6.62	11.20	10.77	109.0	31.0	*****	5.2	394.0	119.0	0.0	41.	6.6
1.	36.14	7.69	7.45	11.23	10.91	203.0	52.0	158.0	14.4	21.6	190.0	0.0	25.	2.8
1.	36.13	7.69	7.45	11.21	10.98	200.0	55.0	192.0	14.4	25.2	190.0	0.0	26.	3.0
1.	36.12	5.13	4.66	11.20	10.98	127.0	38.0	*****	4.4	450.0	127.0	0.0	42.	6.9
1.	36.11	5.13	4.66	11.21	10.98	125.0	39.0	*****	4.1	350.0	134.0	0.0	36.	6.3
1.	36.10	5.13	5.17	11.22	11.10	217.0	63.0	180.0	13.2	21.2	225.0	0.0	21.	3.1
1.	36.09	5.13	5.17	11.20	11.08	209.0	64.0	210.0	12.4	24.0	194.0	0.0	26.	3.7
2.	36.17	24.00	0.0	0.0	10.70	83.0	51.0	*****	5.7	*****	118.0	0.0	49.	8.3

EXPERIMENT NO.= 37.

EFFECT OF VARIOUS SLUDGE CONCENTRATIONS

NA= 48. K= 12. CL= 47. SO4= 45. NO3= 7.5 NO2= 1.5 ORG-C= 5. TOT.P= 8.0 TKN= 2

RN	ID	HRT	MRT	PHR	PHF	ALK	CAF	CAT	MGF	MGT	THF	PO4	COD	NH3
****	37.00	******	******	*****	7.76	157.0	42.0	43.0	20.0	19.8	168.0	7.8	28.	3.1
1.	37.01	5.13	5.17	11.22	10.98	201.0	63.0	176.0	15.0	22.3	190.0	0.0	26.	1.9
1.	37.02	5.13	5.17	11.21	10.98	205.0	67.0	160.0	17.3	20.8	188.0	0.0	26.	2.1
1.	37.03	5.13	4.77	11.21	10.90	168.0	68.0	*****	10.3	203.0	171.0	0.0	26.	2.3
1.	37.04	5.13	4.77	11.20	10.86	169.0	63.0	*****	9.2	214.0	176.0	0.0	28.	2.3
1.	37.05	5.13	4.54	11.20	10.83	160.0	64.0	*****	7.0	329.0	168.0	0.0	28.	2.8
1.	37.06	5.13	4.54	11.22	10.88	162.0	61.0	*****	6.9	340.0	153.0	0.0	26.	2.4
1.	37.07	5.78	4.59	11.21	10.85	156.0	68.0	*****	6.3	540.0	161.0	0.0	31.	3.0
1.	37.08	6.69	5.15	11.24	10.70	142.0	60.0	*****	4.5	615.0	164.0	0.0	42.	2.8
1.	37.09	5.13	4.31	11.21	10.88	136.0	51.0	*****	5.8	390.0	147.0	0.0	46.	2.9
1.	37.10	5.13	4.31	11.21	10.80	127.0	48.0	*****	5.6	425.0	147.0	0.0	28.	2.8
1.	37.11	5.13	4.50	11.21	10.80	136.0	55.0	*****	8.3	315.0	143.0	0.0	26.	2.4
1.	37.12	5.13	4.50	11.21	10.73	134.0	43.0	*****	6.7	310.0	144.0	0.0	26.	2.5
1.	37.13	5.13	4.70	11.21	10.80	142.0	50.0	*****	8.0	248.0	150.0	0.0	26.	2.2
1.	37.14	5.13	4.70	11.22	10.84	142.0	60.0	*****	9.2	234.0	158.0	0.0	25.	2.2
1.	37.15	5.13	4.79	11.22	10.86	149.0	52.0	*****	9.6	194.0	167.0	0.0	27.	2.0
1.	37.16	5.13	4.79	11.19	10.80	148.0	54.0	*****	9.7	188.0	158.0	0.0	21.	1.7

APPENDIX 12

RAW DATA FOR EXPERIMENTS ON STABILIZED LIME-TREATED SECONDARY EFFLUENT*

Raw data collected during the investigation of stabilized lime-treated secondary effluent are listed below. The following codes are used,

ID - Identification code

PKSPCA - Negative logarithm of the calcium carbonate activity product

TEMP - Equilibrium temperature (^{o}C)

PH - pH of stabilized lime-treated secondary effluent

MG - Total dissolved magnesium concentration of the secondary effluent before lime treatment (mg ℓ^{-1} as Mg)

PO_4 - Total dissolved ortho-phosphate concentration of the secondary effluent before lime treatment (mg ℓ^{-1} as P)

COD - Dissolved chemical oxygen demand concentration of the secondary effluent before lime treatment (mg ℓ^{-1} as O)

NH3/4 - Total free and saline ammonia concentration of the stabilized lime-treated secondary effluent (mg ℓ^{-1} as N)

MGO - Total dissolved magnesium concentration of the stabilized lime-treated secondary effluent (mg ℓ^{-1} as Mg)

CODO - Dissolved chemical oxygen demand concentration of the stabilized lime-treated secondary effluent (mg ℓ^{-1} as O)

PKSPMG - Negative logarithm of the magnesium hydroxide activity product

CA - Total dissolved calcium concentration of the secondary effluent before lime treatment (mg ℓ^{-1} as Ca)

CAO - Total dissolved calcium concentration of the stabilized lime-treated secondary effluent (mg ℓ^{-1} as Ca)

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*See Chapter 6, p. 290

ID	PKSPCA	TEMP	PH	MG	PO4	COD	NH3/4	MGO	CODO
1	6.778	22.0	10.92	17.	8.1	26.	4.9	0.0	19.00
2	6.726	22.0	10.97	17.	7.5	30.	3.0	2.00	20.00
3	6.767	22.0	10.91	17.	7.4	28.	4.2	0.0	17.00
4	6.702	22.2	10.45	17.	7.0	39.	4.7	0.0	20.00
5	6.947	23.0	11.20	17.	7.4	31.	4.9	0.0	19.00
6	6.793	22.8	11.00	17.	7.3	27.	5.0	0.0	24.00
7	6.823	20.0	11.10	16.	7.4	32.	4.0	0.0	27.00
8	6.852	19.5	11.00	16.	7.7	33.	3.8	0.0	20.00
9	6.835	19.5	10.80	17.	7.5	39.	3.1	3.00	24.00
10	6.945	19.5	11.22	16.	7.3	30.	3.0	0.0	20.00
11	6.823	19.0	11.18	17.	8.0	29.	3.5	0.0	18.00
12	6.821	19.0	10.95	17.	7.4	33.	4.2	2.00	18.00
13	6.723	18.5	10.83	18.	8.6	31.	5.3	0.0	15.00
14	6.745	18.2	11.00	17.	8.0	33.	4.9	0.0	12.00
15	6.791	19.0	11.10	17.	8.5	32.	4.2	0.0	12.00
16	6.770	18.7	11.10	16.	7.6	28.	3.9	0.0	15.00
17	6.724	18.8	11.03	17.	8.3	31.	4.2	0.0	15.00
18	6.741	19.0	11.00	17.	8.0	28.	5.3	0.0	16.00
19	6.732	19.8	10.76	17.	8.8	30.	7.6	0.0	15.00
20	6.754	19.8	11.30	17.	8.0	26.	6.6	0.0	14.00
21	6.758	19.6	11.23	14.	7.0	31.	5.9	0.0	12.00
22	6.474	19.0	11.20	13.	6.7	29.	5.3	0.0	14.00
23	6.711	19.8	11.20	17.	8.0	22.	4.6	0.0	14.00
24	6.709	19.7	11.41	15.	7.0	22.	4.9	0.0	14.00
25	6.854	20.5	10.80	14.	6.3	20.	2.8	0.0	17.00
26	6.813	20.5	10.72	17.	7.7	20.	2.0	0.0	14.00
27	6.775	20.5	10.85	17.	7.4	20.	1.5	0.0	17.00
28	6.773	20.5	10.90	17.	7.5	21.	1.4	2.00	16.00
29	6.771	20.5	10.70	16.	7.3	19.	1.2	2.00	15.00
30	6.805	20.5	11.40	17.	7.4	18.	1.0	0.0	12.00
31	6.811	18.0	10.80	17.	7.4	30.	1.5	0.0	25.00
32	6.796	19.0	11.41	17.	7.4	32.	1.2	0.0	30.00
33	6.805	19.5	11.40	17.	7.3	32.	1.0	0.0	23.00
34	6.739	19.5	11.00	16.	6.8	32.	0.9	0.0	25.00
35	6.674	20.0	11.28	17.	7.1	34.	0.8	3.00	26.00
36	6.726	20.0	11.42	17.	7.2	34.	0.6	3.00	26.00
37	6.753	12.6	11.09	17.	8.0	20.	2.3	2.00	22.00
38	6.819	13.6	10.86	17.	8.3	23.	2.1	3.00	20.00
39	6.738	13.5	10.69	18.	8.2	20.	1.8	3.00	20.00
40	6.717	13.4	10.52	18.	8.0	20.	1.6	0.0	17.00
41	6.767	12.7	10.75	17.	8.0	22.	1.7	4.00	22.00
42	6.720	12.7	10.90	17.	7.5	22.	2.7	2.00	20.00
43	6.715	13.0	10.70	18.	8.9	28.	8.4	6.00	22.00
44	6.702	12.0	10.72	19.	9.7	32.	8.4	6.00	20.00
45	6.742	12.7	10.62	18.	9.3	31.	7.1	9.00	24.00
46	6.766	10.3	10.70	18.	9.4	29.	6.3	7.00	18.00
47	6.701	10.3	10.50	18.	8.6	26.	6.0	11.00	21.00
48	6.723	10.2	10.30	18.	8.8	27.	6.2	14.00	21.00
49	6.676	16.0	10.95	18.	8.1	32.	6.1	5.00	19.00
50	6.687	17.0	10.75	17.	7.1	30.	5.5	6.00	19.00
51	6.685	16.0	11.05	17.	8.0	30.	5.9	6.00	25.00
52	6.713	17.0	11.00	15.	5.9	28.	4.8	4.00	22.00
53	6.585	16.5	10.95	14.	5.8	30.	4.5	7.00	25.00
54	6.629	17.0	10.60	17.	7.1	29.	4.8	9.00	27.00
55	6.699	13.5	10.35	18.	7.9	29.	6.1	13.00	28.00
56	6.706	14.5	10.42	17.	8.0	32.	5.6	10.00	15.00
57	6.739	19.0	10.45	17.	8.0	30.	4.9	12.00	15.00
58	6.708	19.0	10.38	16.	6.9	26.	4.4	11.00	15.00
59	6.725	18.5	10.35	16.	5.8	26.	4.4	1.00	14.00
60	6.551	18.0	10.62	17.	7.2	28.	4.6	5.00	15.00
61	6.834	18.3	10.72	17.	5.5	22.	4.6	5.00	14.00
62	6.715	18.3	10.73	17.	6.1	28.	7.0	8.00	19.00
63	6.747	18.6	10.86	17.	5.9	25.	6.2	6.00	16.00
65	6.652	19.0	10.45	17.	5.4	22.	5.0	14.00	20.00
66	6.760	19.0	10.45	17.	5.6	22.	5.1	4.00	14.00
67	6.723	12.0	10.50	18.	7.7	13.	5.5	12.00	15.00
68	6.801	13.0	10.29	19.	7.9	25.	5.0	2.00	15.00
69	6.770	15.9	10.39	16.	5.7	18.	4.0	9.00	13.00
70	6.739	15.0	10.32	15.	5.6	18.	4.0	11.00	13.00
72	6.794	15.8	10.09	16.	5.4	18.	4.1	12.00	17.00

ID	PKSPMG	TEMP	PH	CA	P04	COD	NH3/4	CAO	C000
2	10.735	22.0	10.97	35.	7.5	30.	3.0	52.00	20.00
9	11.010	19.5	10.80	35.	7.5	29.	3.1	45.00	24.00
12	10.907	19.0	10.95	37.	7.4	33.	4.2	48.00	18.00
28	10.730	20.5	10.96	37.	7.6	21.	1.4	74.00	16.00
29	11.282	20.5	10.70	37.	7.3	16.	1.2	81.00	15.00
35	10.086	20.0	11.28	38.	7.1	34.	0.8	75.00	26.00
36	9.822	20.0	11.42	37.	7.2	34.	0.8	86.00	26.00
37	11.107	12.6	11.06	38.	8.0	20.	2.3	49.00	22.00
38	11.461	13.6	10.86	38.	8.3	23.	2.1	49.00	30.00
39	11.691	13.5	10.69	38.	8.2	20.	1.8	50.00	20.00
41	11.445	12.7	10.75	36.	8.0	22.	1.7	52.00	22.00
42	11.456	12.7	10.90	36.	7.5	22.	2.7	58.00	20.00
43	11.381	13.0	10.70	41.	8.9	28.	8.4	48.00	22.00
44	11.406	12.0	10.72	41.	9.7	32.	8.4	51.00	20.00
45	11.381	12.7	10.62	40.	9.2	21.	7.1	46.00	24.00
46	11.512	10.3	10.70	40.	9.4	29.	6.2	40.00	18.00
47	11.665	10.3	10.50	40.	8.6	26.	6.0	56.00	21.00
49	11.362	16.0	10.65	40.	8.1	32.	6.1	51.00	18.00
50	11.013	17.0	10.75	40.	7.1	30.	5.5	52.00	18.00
51	10.498	16.0	11.05	39.	8.0	30.	5.9	52.00	25.00
52	10.683	17.0	11.00	40.	5.9	28.	4.8	57.00	22.00
53	10.600	16.5	10.95	39.	5.8	30.	4.5	64.00	25.00
54	10.550	17.0	10.90	39.	7.1	29.	4.8	59.00	27.00
60	11.263	19.0	10.62	39.	7.2	23.	4.6	65.00	15.00
61	11.010	18.3	10.72	42.	5.5	22.	4.6	47.00	14.00
62	10.834	18.3	10.73	42.	6.1	33.	7.0	51.00	18.00
63	10.670	18.6	10.86	40.	5.8	25.	6.3	52.00	16.00
67	11.144	12.0	10.50	41.	7.7	18.	5.5	47.00	15.00

APPENDIX 13

RAW DATA FOR EXPERIMENTS ON STABILIZED RECARBONATED EFFLUENT*

Raw data collected during the investigation of stabilized recarbonated effluent are listed below. The following codes are used,

ID - Identification code
PKSPCA - Negative logarithm of the calcium carbonate activity product
TEMP - Equilibrium temperature (^{o}C)
PH - pH of stabilized recarbonated effluent
NH3/4 - Total free- and saline ammonia concentration of the stabilized recarbonated effluent (mg ℓ^{-1} as N)

Raw data for influent to the recarbonation process, i.e. ammonia stripping tower effluent, are also listed. The following codes are used,

DATE - Date sample was taken
TEMP - Effluent temperature (^{o}C)
PHR - Effluent pH
Alk - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)
Ca(F) - Residual total dissolved calcium (mg ℓ^{-1} as Ca)

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*See Chapter 6, p. 306

ID	PKSPCA	TEMP	PH	NH3/4
1	6.854	22.0	10.32	3.3
2	7.615	22.2	9.55	3.1
3	7.176	21.0	10.10	3.2
4	7.040	20.5	10.32	9.0
5	7.903	22.8	9.20	2.9
6	7.066	22.9	10.85	3.2
7	7.052	23.0	10.52	3.5
8	7.237	22.5	9.99	4.2
9	7.203	21.5	10.11	4.8
10	7.445	21.0	8.80	5.3
11	7.791	20.5	9.10	4.9
12	7.160	20.0	10.40	4.4
13	7.751	20.0	9.30	4.2
14	7.487	19.2	9.80	3.5
15	7.192	20.5	9.85	3.0
16	7.853	22.0	8.69	2.5
17	7.824	21.5	8.90	2.3
18	7.942	20.1	8.85	2.2
19	7.843	21.0	9.09	2.2
20	7.999	23.2	8.70	2.1
21	8.380	26.0	8.20	1.8
22	7.939	27.5	8.69	1.7
23	7.886	29.5	8.80	2.2
24	7.069	28.0	10.00	5.0
25	7.818	29.0	8.84	3.0
26	8.124	26.0	8.66	3.4
27	7.817	24.0	9.10	3.5
28	7.447	23.5	9.70	3.6
29	7.580	21.0	9.39	3.6
30	7.454	19.0	9.70	3.5
31	7.475	18.5	9.89	3.7
32	7.674	21.0	9.40	3.4
33	7.713	21.5	9.32	3.3
34	7.689	20.8	9.49	3.0
35	7.645	22.0	9.49	3.9
36	7.578	24.0	9.60	5.0
37	7.381	22.7	9.69	5.4
38	7.384	22.0	9.70	5.8
39	7.069	21.0	9.80	5.3
40	7.656	20.0	9.25	5.4
41	7.661	19.0	9.21	5.2
42	7.579	19.0	9.50	5.1
43	7.588	18.9	9.51	4.7
44	7.508	18.5	9.57	3.9
45	7.623	27.6	9.45	3.3
46	7.600	17.0	9.32	3.8
47	7.872	19.0	9.02	3.7
48	7.711	19.3	9.49	4.5
49	7.806	20.0	9.20	5.2
50	8.038	20.1	8.90	5.6
51	7.733	20.0	9.41	5.5
52	7.130	20.0	10.50	1.5
53	7.261	20.0	10.34	1.6
54	7.280	19.5	10.29	1.6
55	7.349	20.0	10.21	1.6
56	7.094	20.0	9.50	1.6
57	7.547	20.2	9.72	1.6
58	7.446	21.7	9.82	1.6
59	7.494	23.0	9.69	1.2
60	7.522	23.0	9.58	1.7

Ammonia Stripping tower effluent (6A)*

DATE	TEMP	PHR	ALK	CA(F)
31/10/74	23,0	11,49	190	/77
	22.5	11,39	178	72
	22.5	11,40	170	68
	22.0	11,54	199	77
1/11/74	22.8	11,59	244	94
	22.5	11,10	149	57
	22.8	11,48	205	80
	23.0	11,43	210	85
	23.0	11,40	204	85
	23.0	11,41	206	80
4/11/74	20,3	11,22	129	54
	22.7	11,42	153	67
	22.3	11,46	165	70
	22.0	11,50	181	71
	23.0	11,50	180	67
	23.5	11,45	178	81
	24.5	11,40	168	77
	25.5	11,20	154	73
	26.0	11,15	148	73
	25.0	11,21	154	71
	24.0	11,30	164	79
	24.0	11,30	164	74
5/11/74	23,5	11,30	161	69
	23.0	11,29	152	63
	22.5	11,27	157	65
	22.9	11,30	158	72
	23.5	11,32	104	70
	24.0	11,42	178	80
	25.5	11,43	188	80
	27.1	11,31	175	76
	25.5	11,30	176	64
	25.0	11,31	162	65
	25.0	11,21	170	63
	24.0	11,30	170	68
	24.0	11,25	168	68
	23.5	11,23	158	65
Arithmetic Ave. (N = 36)	23.6	11,35	171	72

*Mg not measured but from past experience usually $\leq 1 mg\ \ell^{-1}$ as Mg

APPENDIX 14

RAW DATA FOR EVALUATION OF FULL-SCALE LIME TREATMENT ON THE STANDER PLANT - LIME REACTOR STUDY*

Raw data collected during the investigation of lime treatment in the full-scale lime reactor are listed below. The following codes are used,

SN - Sample identification code

A - Secondary effluent prior to lime treatment

B,C,D - Lime reactor effluent

E,F - Stabilized (24h) lime reactor effluent

LSF - Lime slurry flow ($\ell\ min^{-1}$)

LSC - Lime slurry concentration ($g\ \ell^{-1}$)

SS - Suspended solids ($mg\ \ell^{-1}$)

TEMP - Lime reactor effluent temperature

PHR - Lime reactor effluent pH

PHF - pH of filtered lime reactor effluent

ALK - Total alkalinity ($mg\ \ell^{-1}$ as $CaCO_3$)

CAT - Total calcium ($mg\ \ell^{-1}$ as Ca)

CAF - Total dissolved calcium ($mg\ \ell^{-1}$ as Ca)

MGF - Total dissolved magnesium ($mg\ \ell^{-1}$ as Mg)

NH3 - Total free- and saline ammonia ($mg\ \ell^{-1}$ as N)

PO_4 - Total dissolved ortho-phosphate ($mg\ \ell^{-1}$ as P)

COD - Total dissolved chemical oxygen demand ($mg\ \ell^{-1}$ as O)

HTE - Humus tank effluent (secondary effluent), daily analyses for cations and anions

Na - Total dissolved sodium ($mg\ \ell^{-1}$ as Na)

K - Total dissolved potassium ($mg\ \ell^{-1}$ as K)

Cl - Total dissolved chloride ($mg\ \ell^{-1}$ as Cl)

SO_4 - Total dissolved sulphate ($mg\ \ell^{-1}$ as SO_4)

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*See Chapter 5, Section 2.2

NO_3 - Total dissolved nitrates (mg ℓ^{-1} as N)
Date - Date sample(s) was taken

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EVALUATION OF FULL SCALE LIME TREATMENT - STANDER PLANT LIME REACTOR

SN	LSF	LSC	SS	TEMP	PHR	PHF	ALK	CAT	CAF	MGF	NH3	PO4	COD	HTE	DATE
1A				22,4	-	7,70	141		36	18	14,6	6,0	40		
1 B,C,D	26	59,7	319	22,1	-	11,32	221	210	90	3,2	4,7	< 0,1	29	Na=54 K=11,4 NO_3=10,0	6.5.74
2A				22,2	-	7,72	144		34	18	7,4	5,2	42		
2 B,C,D	24	63,4	363	21,8	-	11,29	231	220	90	2,1	5,3	< 0,1	22		
3A				22,8	-	7,65	146		36	18	8,0	5,6	42		
3 B,C,D	24	42,7	267	22,5	-	10,90	164	160	55	9,5	5,6	< 0,1	25		
4A				20,0	-	7,83	148		33	17,2	6,3	6,3	34		
4 B,C,D	28	40,9	218	19,5	-	10,95	180	170	55	10,0	5,0	0,1	27		
5A				21,0	-	7,80	148		33,8	17,5	7,3	7,1	43	Na=54 K=13,2 Cℓ=46 SO_4=50 NO_3= 8,6	
5 B,C,D	28	40,6	269	20,2	-	11,05	181	180	55	8,8	5,0	< 0,1	25		7.5.74
6A				22,0	-	7,80	151		33,8	17,5	7,5	7,1	44		
6 B,C,D	28	40,4	290	20,3	11,14	11,08	182	180	57,5	8,8	5,0	< 0,1	26		
7A				21,8	-	7,89	139		33,8	16,3	5,6	5,9	46		
7 B,C,D	34	41,9	296	21,2	11,16	11,16	187	200	67,5	6,3	5,0	0,1	26		
8A				21,5	-	7,93	148		35,0	17,5	6,3	5,8	35		
8 B,C,D	52	30,1	359	21,2	11,30	11,30	212	230	82,5	2,5	6,3	0,1	24	Na=55 K=12,8 Cℓ=51 SO_4=50 NO_3= 8,6	
9A				21,2		7,88	160		37,5	17,5	8,6	5,5	39		8.5.74
9 B,C,D	52	34,4	383	21,1	11,46	11,40	260	230	102,5	1,3	7,6	< 0,1	25		
10A				21,1		8,06	170		37,5	18,8	10,1	6,3	38		
10 B,C,D	45	36,7	369	20,8	11,25	11,19	200	240	70,0	5,0	8,8	0,2	33		

Base flow 4,54 Mℓ d^{-1}; Air flow 7m^3 min^{-1}; No sludge recirculation

EVALUATION OF FULL SCALE LIME TREATMENT - STANDER PLANT LIME

REACTOR

	SN	LSF	LSC	SS	TEMP	PHR	PHF	ALK	CAT	CAF	MGF	NH3	PO4	COD	HTE	DATE
	11A				19,0		7,92	132		35,0	17,5	3,1	5,4	33	) Na=53	
11	B,C,D	23	43,0	256	18,0	11,02	10,94	164	160	57,5	10,0	2,5	<0,1	23	) K=12,0	9.5.74
	12A				20,1		7,87	140		35,0	17,5	4,5	5,3	30	) Cℓ=50	
12	B,C,D	29	33,4	225	19,9	10,80	10,72	159	150	50,0	12,5	3,5	<0,1	24	) SO_4=49	
	13A				20,8		7,85	146		36,3	17,5	6,3	5,1	39	) NO_3=8,0	
13	B,C,D	35	27,7	211	20,5	10,82	10,67	166	150	50,0	12,5	5,0	<0,1	25	)	
	14A				20,7		7,98	165		37,5	18,8	11,4	5,6	38	)	
14	B,C,D	45	26,2	345	20,1	11,03	10,98	189	200	60,0	8,8	9,0	<0,1	25	)	
	15A				20,6		7,80	122		36,3	17,5	5,4	7,0	40	) Na=48	
15	B,C,D	58	19,7	255	19,4	11,09	11,05	174	170	70,0	8,8	4,0	<0,1	26	) K=13,8	
15	E,F				19,9		10,98	120		60,0	1,3	4,3	<0,1	24	) Cℓ=46,0	13.5.74
	16A				20,8		7,87	130		37,5	18,8	6,3	6,6	40	) SO_4=50,0	
16	B,C,D	58	20,7	301	20,2	11,10	11,07	181	190	72,5	7,5	5,1	<0,1	23	) NO_3=12,8	
16	E,F				21,0		11,03	132		65,0	<1,3	5,1	<0,1	44	)	
	17A				21,0		7,76	133		40,0	18,8	7,8	6,6	36	)	
17	B,C,D	58	22,7	302	20,4	11,09	11,09	173	200	70,0	7,5	5,6	<0,1	23	)	
17	E,F				22,8		11,03	136		67,5	<1,3	5,8	<0,1	21	)	
	18A				18,0		7,65	140		37,5	17,5	7,8	8,1	35	)	
18	B,C,D	58	25,1	344	17,8	11,25	11,19	191	220	75,0	5,0	5,3	<0,1	23	) Na=55	
18	E,F,				17,4		11,31	164		67,5	<1,3	5,4	0,6	25	) K=14,0	
	19A				19,7		7,73	135		40,0	17,5	5,8	7,9	35	) Cℓ=51,0	14.5.74
19	B,C,D	58	26,3	337	19,2	11,32	11,26	212	230	87,5	3,8	3,6	<0,1	23	) SO_4=53,0	
19	E,F,				18,2		11,32	197		82,5	<1,3	4,0	0,4	23	) NO_3=11,4	
	20A				21,6		7,82	142		37,5	18,8	7,3	7,6	35	)	
20	B,C,D	52	25,5	334	20,3	11,20	11,18	188	210	75,0	6,3	4,9	<0,1	23	)	
20	E,F				19,0		11,18	155		65,0	<1,3	4,9	<0,1	29	)	

APPENDIX 15

RAW DATA FOR EVALUATION OF THREE MODES OF LIME TREATMENT ON THE FULL-SCALE PLANT*

Raw data collected during the evaluation of three modes of lime treatment on the full-scale plant are listed below. The following codes are used,

DATE - Date sample was taken
TIME - Time of day sample was taken
COND - Condition of test, i.e. 1, 2 or 3 as indicated in heading to each table
TURB - Turbidity (Jackson turbidity units)
TEMPR - Temperature of the clarifier effluent (^{o}C)
PHRAW - pH of the clarifier effluent
TEMPF - Temperature of filtered clarifier effluent (^{o}C)
PHFILT - pH of filtered clarifier effluent
ALKF - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)
CA(A) - Total calcium (mg ℓ^{-1} as Ca)
MG(A) - Total magnesium (mg ℓ^{-1} as Mg)
O-P(A) - Total ortho-phosphate (mg ℓ^{-1} as P)
CODA - Total COD (mg ℓ^{-1} as O)
NH3A - Total free-and saline ammonia (mg ℓ^{-1} as N)
TOTHA - Total hardness (mg ℓ^{-1} as $CaCO_3$)
CA(F) - Total dissolved calcium (mg ℓ^{-1} as Ca)
MG(F) - Total dissolved magnesium (mg ℓ^{-1} as Mg)
OrP(F) - Total dissolved ortho-phosphate (mg ℓ^{-1} as P)
CODF - Total dissolved COD (mg ℓ^{-1} as O)
NH3F - Total dissolved free-and saline ammonia (mg ℓ^{-1} as N)
TOTHF - Dissolved total hardness (mg ℓ^{-1} as $CaCO_3$)
IDENT - Sample identification code

*See Chapter 5, Section 3.1

NDIX 15

ATION OF EXCESS LIME PROCESS AT THE STANGER WATER RECLAMATION PLANT

TANK EFFLUENT (1A)

			TIME	COLOUR	TURB	TEMPS	PHRAW	TEMPF	PHFILT	ALKF	CA(A)	MG(A)	O-P(A)	COD(A	NH3(A	TOTHA	CA(F)	MG(F)	O-P(F)	COLOUR	TURB	TEMP	
74		1		5.1	17.5	7.48	17.0	7.62	130.	39.	17.	8.00	32.	4.7	169.	37.	17.	8.10				
74	14	1		5.0	20.0	7.49	17.8	7.67	128.	37.	17.	7.90	31.	5.0	158.	35.	17.	7.90				
74	14	1		5.0	20.0	7.45	20.5	7.60	130.	36.	17.	7.40	32.	4.1	159.	36.	17.	7.40				
74	15	1		5.0	20.0	7.49	21.0	7.62	132.	37.	18.	7.40	42.	4.6	164.	36.	17.	7.40				
74	16	1		5.0	20.0	7.48	21.0	7.70	113.	38.	17.	7.60	33.	5.1	167.	37.	17.	7.40				
74	17	1		4.0	17.5	7.52	20.5	7.53	105.	36.	17.	7.30	33.	4.7	169.	37.	17.	7.40				
74	0	2		4.5	17.0	7.56	17.2	7.65	126.	37.	16.	7.40	34.	5.7	159.	36.	16.	7.40				
74		2		3.9	16.0	7.50	16.2	7.56	123.	37.	16.	8.00	34.	5.7	161.	36.	16.	7.70				
74	01	2		3.5	16.0	7.50	16.4	7.64	122.	36.	17.	7.80	30.	5.1	159.	35.	17.	7.40				
74	02	2		3.5	15.7	7.57	15.5	7.60	120.	37.	16.	7.60	35.	4.9	160.	34.	16.	7.50				
74	03	2		3.0	15.0	7.60	15.3	7.63	122.	36.	17.	8.00	32.	5.2	162.	34.	17.	7.50				
74	04	2		3.0	14.8	7.65	14.8	7.69	124.	37.	17.	7.80	40.	4.8	164.	35.	17.	7.50				
74	05	2		3.0	15.0	7.52	15.0	7.62	127.	38.	18.	8.50	30.	5.2	170.	35.	17.	7.60				
74	06	2		3.0	14.8	7.60	14.8	7.68	122.	37.	17.	7.50	31.	4.8	164.	36.	17.	7.50				
74	07	2		3.0	15.0	7.63	15.0	7.69	121.	36.	18.	8.50	32.	4.8	170.	37.	17.	7.60				
74	08	2		3.0	15.0	7.65	15.0	7.71	119.	37.	18.	7.90	31.	5.9	164.	37.	17.	7.60				
74	09	2		3.0	15.0	7.70	15.0	7.70	121.	37.	17.	8.50	34.	6.0	170.	36.	17.	7.70				
74	10	2		3.0	15.0	7.70	14.8	7.70	120.	36.	17.	8.50	33.	5.6	170.	37.	17.	7.70				
74	11	2		3.0	15.0	7.70	15.0	7.70	120.	36.	16.	8.50	34.	7.4	170.	37.	17.	7.80				
74	12	2		3.0	17.0	7.65	17.0	7.65	122.	37.	17.	8.50	30.	5.5	160.	37.	17.	7.80				
74	13	2		3.0	17.5	7.65	17.5	7.65	114.	38.	14.	7.90	28.	6.0	164.	38.	14.	7.80				
74	14	2		3.0	16.0	7.75	16.0	7.75	112.	38.	14.	8.50	29.	7.5	168.	36.	14.	7.80				
74	15	2		3.0	15.5	7.65	15.5	7.65	118.	37.	16.	8.60	28.	6.6	159.	37.	17.	7.80				
74	16	2		3.0	15.0	7.60	15.0	7.60	111.	36.	15.	8.50	28.	7.2	155.	37.	17.	7.80				
74	17	2		3.0	15.5	7.55	15.5	7.55	105.	40.	14.	8.20	34.	8.0	152.	37.	17.	7.80				
74	0	3		3.0	16.0	7.60	16.0	7.60	111.	37.	16.	7.70	28.	6.0	154.	37.	17.	7.80				
74	01	3		3.0	17.0	7.65	17.0	7.69	124.	36.	17.	7.60	32.	5.5	159.	37.	17.	7.80				
74	02	3		3.0	17.0	7.76	17.0	7.76	120.	37.	17.	7.60	32.	5.5	159.	37.	17.	7.80				
74	03	3		3.0	16.0	7.60	16.2	7.46	108.	37.	16.	7.50	30.	5.2	158.	37.	16.	7.80				
74	04	3		3.0	16.0	7.60	16.0	7.60	106.	37.	17.	7.60	31.	5.0	159.	37.	17.	7.80				
74	05	3		3.0	16.5	7.70	17.0	7.70	107.	40.	17.	7.50	34.	5.7	170.	38.	17.	7.80				
74	06	3		3.0	17.0	7.70	17.0	7.70	108.	38.	17.	7.60	34.	6.1	167.	38.	17.	7.80				
74	07	3		4.0	17.5	7.65	17.0	7.65	108.	39.	17.	7.50	34.	5.9	170.	38.	17.	7.80				
74	08	3		3.0	17.0	7.60	16.8	7.60	106.	38.	16.	8.50	34.	5.9	169.	38.	16.	7.80				
74	09	3		3.0	16.5	7.55	16.5	7.59	108.	38.	17.	7.60	36.	6.7	170.	38.	17.	7.80				
74	10	3		3.0	16.5	7.55	16.5	7.59	108.	38.	17.	7.60	35.	6.6	167.	38.	17.	7.80				
74	11	3		3.0	16.5	7.55	16.5	7.59	110.	38.	17.	7.70	28.	6.5	164.	38.	17.	7.80				
74	12	3		3.0	16.0	7.60	16.0	7.68	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	13	3		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	14	3		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	15	3		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	16	3		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	17	3		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	0	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	01	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	02	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	03	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	04	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	05	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	06	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	07	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	08	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	09	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	10	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	11	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	12	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	13	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	14	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	15	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	16	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	17	4		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	0	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	01	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	02	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	03	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	04	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	05	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	06	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	07	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	08	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	09	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	10	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	11	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	12	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	13	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	14	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	15	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	16	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	17	5		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	0	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	01	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	02	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	03	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	04	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	05	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	06	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	07	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	08	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	09	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	10	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	11	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	12	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	13	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	14	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	15	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	16	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	17	6		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	0	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	01	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	02	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	03	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	04	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	05	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	06	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	07	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	08	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	09	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	10	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	11	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	12	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	13	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	14	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	15	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	16	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	17	7		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	0	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	01	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	02	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	03	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	04	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	05	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	06	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	07	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	08	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	09	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	10	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	11	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	12	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	13	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	14	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	15	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	16	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				
74	17	8		4.0	15.4	7.60	14.8	7.78	120.	40.	16.	8.00	28.	6.8	167.	38.	16.	7.80				

FULL SCALE PRIMARY CLARIFIER EFFLUENT QUALITY : CONDITION 1 - REACTOR AND CLARIFIER, WITH SLUDGE RECIRCULATION BEFORE THE REACTOR

DATE	TIME	COND.	TURB	TEMPR	PHRAW	TEMPF	PHFILT	ALKF	CA(A)	MG(A)	O-P(A)	CODA	NH3A	TOTHA	CA(F)	MG(F)	O-P(F)	CODF	NH3F	TOTHF	IDENT
28/ 8/74	9	1	1.7	17.5	11.20	17.5	11.10	138.	66.	3.	0.0	23.	4.3	172.	62.	3.	0.0	17.	4.4	169.	1 3A
28/ 8/74	12	1	3.5	18.5	11.29	19.5	11.20	140.	69.	2.	0.0	22.	3.8	178.	67.	2.	0.0	18.	3.8	172.	2 3A
28/ 8/74	14	1	4.0	19.7	10.92	20.8	10.89	124.	64.	3.	0.0	21.	3.0	181.	61.	3.	0.0	15.	3.0	169.	3 3A
28/ 8/74	15	1	2.5	19.8	10.96	20.8	10.89	130.	61.	4.	0.0	20.	3.2	169.	60.	4.	0.0	17.	3.3	169.	4 3A
28/ 8/74	16	1	3.5	19.8	10.95	21.0	10.91	131.	63.	5.	0.0	23.	3.4	178.	62.	3.	0.0	17.	3.4	172.	5 3A
28/ 8/74	17	1	2.9	19.5	10.91	20.5	10.82	123.	63.	4.	0.0	24.	3.6	175.	60.	3.	0.0	17.	3.5	168.	6 3A
31/ 8/74	68	1	1.0	16.7	11.36	16.0	11.25	146.	75.	2.	0.0	18.	6.6	191.	71.	2.	0.0	15.	6.6	182.	7 3A
31/ 8/74	9	1	2.0	17.0	11.31	17.0	11.20	120.	75.	2.	0.0	23.	5.6	190.	68.	1.	0.0	15.	5.8	174.	8 3A
31/ 8/74	10	1	1.6	17.5	11.27	17.5	11.20	126.	71.	0.	0.0	15.	5.0	170.	76.	0.	0.0	21.	5.1	187.	9 3A
31/ 8/74	11	1	1.2	18.0	11.30	17.8	11.26	144.	76.	0.	0.0	18.	4.9	187.	72.	0.	0.0	15.	4.8	182.	10 3A
31/ 8/74	12	1	1.0	18.0	11.39	18.5	11.32	144.	81.	0.	0.0	18.	4.5	211.	76.	0.	0.0	13.	4.3	198.	11 3A
31/ 8/74	13	1	0.9	19.5	11.25	19.0	11.20	145.	76.	2.	0.0	16.	3.6	191.	72.	0.	0.0	16.	3.6	180.	12 3A
3/ 9/74	8	1	2.1	16.0	10.93	15.5	10.76	133.	63.	9.	0.0	15.	2.1	182.	60.	8.	0.0	13.	2.0	187.	13 3A
3/ 9/74	9	1	1.2	16.0	10.84	16.0	10.71	120.	64.	8.	0.0	12.	2.0	189.	60.	8.	0.0	12.	1.8	178.	14 3A
3/ 9/74	10	1	1.1	16.5	10.96	16.5	10.85	131.	64.	9.	0.0	15.	1.8	192.	59.	9.	0.0	12.	1.5	182.	15 3A
3/ 9/74	11	1	2.8	17.0	10.79	17.5	10.63	112.	56.	10.	0.0	15.	1.5	182.	54.	10.	0.0	16.	1.4	172.	16 3A
3/ 9/74	12	1	2.0	17.5	10.69	18.5	10.52	111.	53.	10.	0.0	14.	1.4	169.	50.	10.	0.0	15.	1.3	163.	17 3A
3/ 9/74	13	1	1.1	18.0	10.81	19.0	10.72	125.	61.	9.	0.0	15.	1.5	181.	57.	8.	0.0	12.	1.4	175.	18 3A
6/ 9/74	8	1	3.0	15.3	10.56	13.8	10.45	166.	66.	14.	0.0	24.	5.0	222.	64.	13.	0.0	23.	4.3	215.	19 3A
6/ 9/74	9	1	2.1	15.5	10.55	14.5	10.40	166.	67.	15.	0.0	23.	4.9	228.	61.	14.	0.0	20.	4.8	208.	20 3A
6/ 9/74	10	1	2.7	16.0	10.55	16.0	10.50	167.	63.	14.	0.0	26.	4.6	220.	61.	14.	0.0	21.	4.4	210.	21 3A
6/ 9/74	10	1	2.3	16.0	10.55	16.0	10.45	158.	63.	14.	0.0	24.	4.3	210.	60.	13.	0.0	22.	4.0	208.	22 3A
6/ 9/74	12	1	2.5	16.5	10.70	16.5	10.60	153.	65.	12.	0.0	28.	4.0	218.	60.	12.	0.0	20.	3.7	197.	23 3A
6/ 9/74	13	1	4.2	17.5	10.55	17.5	10.55	155.	66.	12.	0.0	25.	3.9	210.	60.	12.	0.0	22.	3.7	199.	24 3A

FULL SCALE PRIMARY CLARIFIER EFFLUENT QUALITY : CONDITION 2 - REACTOR AND CLARIFIER, WITH SLUDGE RECIRCULATION AFTER THE REACTOR

DATE	TIME	COND.	TURB	TEMPR	PHRAW	TEMPF	PHFILT	ALKF	CA(A)	MG(A)	O-P(A)	CODA	NH3A	TOTHA	CA(E)	MG(E)	O-P(E)	CODE	NH3E	TOTHE	IDENT
29/ 8/74	8	2	2.0	17.5	10.88	17.0	10.80	139.	57.	7.	0.0	12.	3.1	173.	58.	7.	0.0	16.	3.3	176.	1 3A
29/ 8/74	9	2	2.0	18.0	11.00	17.8	10.98	126.	65.	5.	0.0	26.	2.9	176.	61.	4.	0.0	19.	3.0	168.	2 3A
29/ 8/74	10	2	2.5	18.1	11.00	18.8	10.89	126.	62.	5.	0.0	27.	2.8	177.	60.	5.	0.0	20.	2.6	169.	3 3A
29/ 8/74	11	2	2.5	19.0	11.00	19.3	10.91	134.	60.	7.	0.0	20.	2.5	178.	57.	6.	0.0	18.	2.5	171.	4 3A
29/ 8/74	12	2	3.0	19.0	11.05	19.7	10.95	136.	61.	6.	0.0	20.	2.4	178.	58.	6.	0.0	19.	2.4	171.	5 3A
29/ 8/74	13	2	2.3	19.5	11.10	20.0	11.05	134.	63.	5.	0.0	19.	2.5	173.	60.	4.	0.0	18.	2.5	168.	6 3A
1/ 9/74	8	2	2.1	16.5	11.22	15.5	11.18	115.	71.	4.	0.0	20.	2.3	190.	66.	3.	0.0	20.	2.3	178.	7 3A
1/ 9/74	9	2	1.9	17.0	11.20	16.0	11.10	117.	71.	4.	0.0	20.	2.6	193.	66.	3.	0.0	18.	2.0	176.	8 3A
1/ 9/74	10	2	1.8	17.5	11.10	17.0	11.02	128.	67.	5.	0.0	20.	1.6	180.	62.	4.	0.0	20.	1.6	173.	9 3A
1/ 9/74	11	2	2.0	18.0	11.05	17.8	11.00	115.	66.	5.	0.0	21.	1.3	182.	62.	5.	0.0	20.	1.3	173.	10 3A
1/ 9/74	12	2	1.9	18.0	11.25	18.2	11.20	124.	74.	3.	0.0	22.	1.0	192.	70.	2.	0.0	22.	1.0	178.	11 3A
1/ 9/74	13	2	1.8	18.5	11.30	19.0	11.28	118.	77.	2.	0.0	23.	0.8	198.	72.	1.	0.0	20.	0.8	182.	12 3A
4/ 9/74	8	2	1.2	15.4	10.82	15.0	10.68	151.	60.	12.	0.0	18.	6.3	198.	56.	12.	0.0	15.	6.1	182.	13 3A
4/ 9/74	9	2	1.3	15.7	10.90	15.7	10.63	153.	62.	13.	0.0	17.	6.0	192.	56.	12.	0.0	15.	5.9	182.	14 3A
4/ 9/74	10	2	1.7	15.9	10.80	15.5	10.65	155.	61.	13.	0.0	19.	5.7	197.	54.	13.	0.0	17.	5.5	178.	15 3A
4/ 9/74	11	2	1.7	15.9	10.80	15.8	10.64	149.	61.	13.	0.0	22.	5.0	202.	56.	13.	0.0	20.	4.9	193.	16 3A
4/ 9/74	12	2	1.3	15.8	10.72	15.7	10.39	144.	61.	13.	0.0	21.	4.6	212.	56.	13.	0.0	19.	4.4	190.	17 3A
4/ 9/74	13	2	1.7	16.0	10.77	16.0	10.57	146.	61.	13.	0.0	21.	4.5	203.	54.	13.	0.0	20.	4.3	190.	18 3A
7/ 9/74	8	2	2.4	16.0	10.55	15.0	10.50	148.	57.	13.	0.0	18.	5.6	177.	56.	13.	0.0	15.	5.5	177.	19 3A
7/ 9/74	9	2	2.0	16.5	10.70	16.2	10.60	125.	57.	11.	0.0	19.	5.6	175.	54.	11.	0.0	17.	5.4	168.	20 3A
7/ 9/74	10	2	1.5	17.0	10.85	16.2	10.73	128.	61.	10.	0.0	14.	5.5	179.	59.	10.	0.0	13.	5.3	168.	21 3A
7/ 9/74	11	2	2.0	17.3	10.80	16.7	10.78	131.	63.	8.	0.0	18.	5.5	163.	60.	8.	0.0	16.	5.3	170.	22 3A
7/ 9/74	12	2	1.4	17.7	10.67	17.4	10.50	129.	60.	10.	0.0	18.	5.0	174.	58.	10.	0.0	15.	4.7	168.	23 3A
7/ 9/74	13	2	2.0	18.1	10.55	18.0	10.41	137.	61.	12.	0.0	18.	4.5	186.	58.	12.	0.0	16.	4.4	180.	24 3A

FULL SCALE PRIMARY CLARIFIER EFFLUENT QUALITY ; CONDITION 3 - CLARIFIER ONLY, i.e. NO REACTOR

DATE	TIME	COND.	TURB	TEMPR	PHPAW	TEMPF	PHFILT	ALKF	CA(A)	MG(A)	O-P(A)	CODA	NH3A	TOTHA	CA(F)	MG(F)	O-P(F)	CODF	NH3F	TOTHF	IDENT
30/ 8/74	8	3	2.0	18.0	11.19	18.0	11.09	132.	67.	4.	0.0	20.	4.1	176.	64.	4.	0.0	17.	4.2	177.	1 3A
30/ 8/74	9	3	2.1	18.1	11.10	18.1	11.05	138.	70.	4.	0.0	21.	4.0	180.	65.	3.	0.0	17.	3.8	177.	2 3A
30/ 8/74	10	3	2.3	18.5	11.21	18.5	11.11	144.	72.	4.	0.0	23.	3.6	191.	68.	3.	0.0	15.	3.5	177.	3 3A
30/ 8/74	11	3	2.2	18.6	11.20	19.0	11.11	146.	68.	3.	0.0	18.	3.2	182.	64.	4.	0.0	22.	3.5	178.	4 3A
30/ 8/74	12	3	2.6	19.0	11.19	19.0	11.10	136.	71.	4.	0.0	19.	3.2	191.	67.	3.	0.0	18.	3.1	176.	5 3A
30/ 8/74	13	3	2.6	19.1	11.15	19.9	11.05	130.	70.	5.	0.0	18.	3.4	186.	66.	4.	0.0	15.	3.3	177.	6 3A
2/ 9/74	8	3	1.9	16.5	11.51	17.0	11.49	161.	93.	2.	0.0	26.	1.2	238.	86.	1.	0.0	24.	1.1	210.	7 3A
2/ 9/74	9	3	2.5	16.5	11.44	17.0	11.40	142.	79.	3.	0.0	27.	1.0	197.	75.	2.	0.0	24.	1.0	190.	8 3A
2/ 9/74	10	3	2.4	17.5	11.32	18.0	11.26	123.	73.	3.	0.0	29.	0.9	193.	70.	2.	0.0	23.	0.9	187.	9 3A
2/ 9/74	11	3	1.6	17.8	11.38	18.5	11.30	127.	76.	3.	0.0	27.	0.8	192.	71.	2.	0.0	27.	0.9	185.	10 3A
2/ 9/74	12	3	2.4	18.0	11.30	18.0	11.30	125.	78.	3.	0.0	31.	0.7	210.	72.	3.	0.0	20.	0.7	190.	11 3A
2/ 9/74	13	3	1.8	18.5	11.40	19.7	11.39	132.	77.	3.	0.0	23.	0.6	200.	72.	3.	0.0	20.	0.6	193.	12 3A
5/ 9/74	8	3	2.0	15.5	10.93	14.2	10.77	161.	67.	12.	0.0	20.	5.0	208.	66.	11.	0.0	20.	5.1	221.	13 3A
5/ 9/74	9	3	1.7	15.2	11.00	14.5	10.85	145.	68.	11.	0.0	22.	5.0	212.	67.	10.	0.0	25.	5.8	204.	14 3A
5/ 9/74	10	3	1.7	15.2	11.06	14.7	10.90	152.	70.	9.	0.0	20.	4.9	210.	67.	9.	0.0	19.	4.5	205.	15 3A
5/ 9/74	11	3	2.1	15.3	11.00	14.9	10.95	149.	68.	9.	0.0	20.	4.7	203.	66.	9.	0.0	19.	4.3	208.	16 3A
5/ 9/74	12	3	1.7	15.5	11.06	14.8	10.90	139.	69.	9.	0.0	20.	4.4	211.	67.	8.	0.0	18.	4.0	202.	17 3A
5/ 9/74	13	3	2.0	15.5	11.00	15.1	10.91	132.	71.	9.	0.0	28.	4.5	216.	66.	9.	0.0	16.	4.0	190.	18 3A
9/ 9/74	8	3	2.2	15.0	10.81	14.0	10.80	156.	66.	11.	0.0	17.	4.8	191.	63.	11.	0.0	14.	4.6	175.	19 3A
9/ 9/74	9	3	2.0	15.5	10.80	14.5	10.70	151.	65.	11.	0.0	17.	4.5	191.	65.	11.	0.0	15.	4.5	180.	20 3A
9/ 9/74	10	3	2.3	16.0	10.68	15.5	10.60	151.	68.	13.	0.0	15.	4.3	206.	65.	13.	0.0	13.	4.0	188.	21 3A
9/ 9/74	11	3	2.2	16.5	10.70	16.5	10.60	143.	68.	13.	0.0	13.	3.8	205.	65.	12.	0.0	15.	3.6	190.	22 3A
9/ 9/74	12	3	3.0	17.5	10.71	17.5	10.60	142.	71.	12.	0.0	14.	3.7	214.	66.	12.	0.0	12.	3.5	188.	23 3A
9/ 9/74	13	3	2.0	17.0	10.80	17.8	10.60	134.	67.	11.	0.0	15.	3.5	190.	62.	11.	0.0	13.	3.4	168.	24 3A

APPENDIX 16

RAW DATA FOR EVALUATION OF THE FULL-SCALE LIME TREATMENT SYSTEM - NOVEMBER 1974 STUDY*

Raw data collected during the investigation of full-scale lime treatment, the November 1974 study, are listed below. The following codes are used,

SET - Refers to a set of samples taken at various sampling points on the full-scale plant

TIME - Time of day when sample was taken

SP - Sample point :

- 1 - Secondary effluent
- 2 - Lime reactor effluent
- 3 - Primary clarifier effluent
- 5 - Equalization pond effluent
- 6 - Ammonia stripping tower effluent
- 10 - Secondary clarifier effluent
- 11 - Sand filter effluent
- 14 - Final plant effluent

SN - Sample identification

T(R) - Effluent temperature (^{o}C)

PHR - Effluent pH

T(F) - Temperature of filtered effluent (^{o}C)

PHF - pH of filtered effluent

TA - Total alkalinity (mg ℓ^{-1} as $CaCO_3$)

CAF - Residual total dissolved calcium (mg ℓ^{-1} as Ca)

MGF - Residual total dissolved magnesium (mg ℓ^{-1} as Mg)

NH_3 - Total dissolved free-and saline ammonia (mg ℓ^{-1} as N)

TURB - Turbidity (Jackson turbidity units)

CAT - Total calcium (mg ℓ^{-1} as Ca)

MGT - Total magnesium (mg ℓ^{-1} as Mg)

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*See Chapter 5, Section 4.

FLOW - Base flow through plant (Mℓ d^{-1})

COD - Total dissolved chemical oxygen demand (mg ℓ^{-1} as O)

PO_4 - Total dissolved ortho-phosphate (mg ℓ^{-1} as P)

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SET 1

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
12.15	1.	1.01	25.2	7.74	26.2	7.88	175.	52.	20.3	5.3	******	43.	20.0	2.40	27.	7.4
12.30	2.	1.02	24.6	11.46	25.8	11.36	231.	118.	9.3	4.3	******	3250.	500.0	2.40	26.	2.6
12.45	3.	1.03	24.9	11.22	24.9	11.01	137.	72.	2.3	4.0	******	66.	1.8	2.40	24.	0.1
13.25	5.	1.04	23.9	11.02	24.8	10.97	108.	49.	1.7	2.5	******	51.	1.8	2.40	25.	0.1
13.45	6.	1.05	23.2	10.66	24.6	10.54	68.	34.	1.3	0.2	******	36.	1.6	2.40	27.	0.1
13.55	10.	1.06	23.8	7.40	24.3	7.47	58.	36.	1.5	0.1	0.80	35.	1.7	2.40	27.	0.2
14.05	11.	1.07	23.4	7.22	24.9	7.41	56.	36.	1.5	0.1	0.50	36.	1.7	2.40	21.	0.1
14.20	14.	1.08	25.9	6.76	25.9	6.95	45.	39.	1.7	1.0	0.20	*****	*****	2.40	21.	0.1

SET 2

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
14.35	1.	2.01	25.2	7.73	26.3	7.82	174.	37.	20.4	5.7	******	39.	20.0	2.40	32.	6.7
14.45	2.	2.02	24.9	11.45	25.7	11.38	221.	120.	6.0	4.9	******	3650.	500.0	2.40	21.	1.7
14.55	3.	2.03	24.9	11.36	25.4	11.33	187.	69.	1.4	4.0	******	78.	1.6	2.40	23.	0.3
15.23	5.	2.04	23.4	11.07	25.2	10.98	115.	48.	1.7	2.5	******	50.	1.8	2.40	26.	0.4
15.30	6.	2.05	23.4	10.66	24.8	10.56	57.	35.	1.4	0.1	******	34.	1.6	2.40	23.	0.2
15.40	10.	2.06	23.7	7.45	25.2	7.57	58.	35.	1.5	0.1	0.89	35.	1.6	2.40	24.	0.6
15.50	11.	2.07	23.8	7.04	25.2	7.38	57.	34.	1.7	0.1	0.45	36.	1.6	2.40	20.	0.6
16.00	14.	2.08	26.0	6.84	26.2	7.04	49.	38.	1.7	0.1	0.24	*****	*****	2.40	16.	0.1

SET 3

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
9.00	1.	4.00	23.5	7.69	23.6	7.90	178.	43.	20.8	8.8	******	44.	21.0	2.40	35.	8.4
9.20	2.	5.00	23.4	11.30	23.3	11.06	165.	51.	9.5	5.2	******	3100.	507.5	2.40	25.	0.3
9.50	3.	6.00	23.4	11.11	24.0	11.07	140.	55.	1.9	6.1	******	85.	5.5	2.40	24.	0.2
10.15	5.	7.00	22.4	11.05	23.5	10.98	105.	42.	1.1	3.3	******	47.	1.3	2.40	25.	0.1
10.25	6.	9.00	22.5	10.62	23.4	10.51	52.	31.	0.9	0.9	******	32.	1.1	2.40	24.	0.2
10.35	10.	11.00	22.6	8.82	23.6	7.87	50.	32.	1.0	0.4	0.83	31.	1.2	2.40	20.	1.0
10.45	11.	13.00	22.9	7.34	24.0	7.52	47.	29.	1.0	1.0	0.28	32.	1.0	2.40	19.	0.4
10.50	14.	15.00	24.6	7.05	24.7	7.12	43.	30.	1.3	1.0	0.03	*****	*****	2.40	21.	0.4

SET 4

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
11.00	1.	16.00	24.0	7.74	24.5	7.82	168.	42.	20.4	6.4	******	40.	20.7	2.40	30.	8.0
11.10	2.	18.00	24.9	11.30	24.8	11.12	153.	60.	3.7	6.0	******	3250.	502.7	2.40	30.	0.5
11.20	3.	20.00	24.0	11.10	24.0	11.04	138.	58.	2.1	5.6	******	57.	2.3	2.40	22.	0.3
11.30	5.	22.00	22.7	11.05	23.8	10.99	104.	45.	1.2	3.7	******	44.	1.3	2.40	21.	1.5
11.40	6.	24.00	22.9	10.57	23.8	10.31	52.	29.	1.1	0.4	******	32.	1.3	2.40	21.	1.4
11.50	10.	26.00	23.2	7.63	24.1	7.57	51.	32.	1.2	0.3	0.79	31.	1.2	2.40	23.	1.6
12.00	11.	28.00	23.4	7.31	24.3	7.33	48.	32.	1.2	0.1	0.33	31.	1.2	2.40	26.	1.2
12.05	14.	30.00	25.7	7.10	25.7	7.23	45.	31.	1.4	0.1	0.18	*****	*****	2.40	19.	0.2

SET 5

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
13.35	1.	33.00	25.5	7.76	26.3	7.90	176.	39.	20.4	7.2	******	44.	20.4	2.40	26.	7.7
13.42	2.	35.00	25.0	11.35	26.8	11.25	178.	64.	2.8	5.8	******	4250.	575.0	2.40	23.	0.3
13.55	3.	37.00	25.1	11.09	25.8	10.98	143.	56.	2.0	5.3	******	58.	2.4	2.40	22.	0.6
14.03	5.	39.00	23.5	11.01	24.8	10.87	122.	42.	1.3	3.7	******	45.	1.4	2.40	23.	1.1
14.15	6.	41.00	23.8	10.46	25.1	10.31	68.	31.	1.1	1.0	******	29.	1.2	2.40	25.	0.6
14.25	10.	43.00	23.9	7.68	25.1	7.81	52.	30.	1.2	0.3	0.69	29.	1.2	2.40	21.	0.2
14.33	11.	45.00	24.1	7.24	25.1	7.50	49.	30.	1.2	0.5	0.28	29.	1.2	2.40	22.	0.1
14.40	14.	47.00	27.4	7.01	27.2	7.23	49.	31.	1.3	0.1	0.19	*****	*****	2.40	18.	0.0

SET 6

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
16.35	1.	48.00	25.7	7.67	26.7	7.77	177.	38.	20.4	7.3	******	40.	20.3	2.40	32.	7.5
17.00	2.	50.00	25.4	11.42	26.3	11.35	210.	73.	1.8	5.9	******	3700.	532.5	2.40	23.	0.2
17.10	3.	52.00	25.4	11.17	26.2	11.13	161.	60.	1.2	5.7	******	66.	1.6	2.40	22.	0.2
17.17	5.	54.00	23.6	10.95	24.5	10.87	114.	41.	1.2	3.9	******	44.	1.4	2.40	25.	0.1
17.25	6.	56.00	23.8	10.39	25.1	10.30	60.	29.	0.9	0.6	******	31.	1.2	2.40	22.	0.1
17.33	10.	58.00	24.8	7.24	25.2	7.38	47.	30.	1.0	0.3	0.66	31.	1.2	2.40	21.	0.1
17.42	11.	60.00	24.2	6.99	25.1	7.15	44.	31.	1.2	0.1	0.24	30.	1.3	2.40	23.	0.1
17.50	14.	62.00	27.4	6.93	27.0	7.08	48.	31.	1.3	0.1	0.20	*****	*****	2.40	21.	0.1

SET 7

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
8.40	1.	63.00	24.0	7.70	24.0	7.75	141.	36.	18.3	3.8	******	40.	20.3	2.40	25.	5.6
8.50	2.	65.00	23.4	11.79	23.8	11.71	258.	104.	1.1	3.1	******	5050.	700.0	2.40	15.	0.1
9.00	3.	67.00	23.5	11.68	24.0	11.62	229.	98.	1.3	2.5	******	87.	0.8	2.40	19.	0.1
9.08	5.	69.00	22.6	11.59	23.4	11.56	178.	84.	0.5	2.5	******	100.	1.5	2.40	17.	0.1
9.18	6.	71.00	22.6	11.36	23.1	11.31	118.	66.	0.3	2.4	******	60.	0.4	2.40	17.	0.1
9.25	10.	73.00	22.6	8.77	23.2	8.72	102.	62.	0.7	0.7	1.10	61.	0.4	2.40	19.	0.2
9.35	11.	75.00	22.8	7.93	23.1	7.96	94.	58.	0.5	0.1	0.58	57.	0.5	2.40	14.	0.1
9.45	14.	77.00	23.4	7.13	23.5	7.34	84.	52.	1.0	0.1	0.33	56.	1.0	2.40	16.	0.1

SET 8

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
10.45	1.	78.00	24.4	7.72	25.3	7.88	149.	38.	19.3	3.0	******	40.	19.0	2.40	21.	5.4
10.55	2.	80.00	24.2	11.57	24.5	11.50	200.	81.	11.3	3.1	******	5250.	731.3	2.40	15.	0.2
11.05	3.	82.00	24.1	11.67	24.5	11.64	231.	112.	0.8	3.1	******	120.	1.5	2.40	17.	0.1
11.15	5.	84.00	23.4	11.57	23.8	11.54	184.	92.	1.0	2.5	******	89.	0.7	2.40	18.	0.1
11.25	6.	86.00	23.4	11.36	23.8	11.33	117.	62.	0.7	0.6	******	69.	0.5	2.40	16.	0.1
11.35	10.	88.00	24.4	8.63	24.0	8.57	103.	62.	0.8	0.4	2.80	69.	0.8	2.40	16.	0.1
11.45	11.	90.00	23.8	8.13	24.0	8.14	100.	56.	1.1	0.2	1.20	59.	0.8	2.40	15.	0.1
11.55	14.	92.00	25.1	7.10	24.9	7.35	68.	54.	1.2	0.1	0.34	56.	0.9	2.40	15.	0.1

SET 9

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
12.00	1.	93.00	24.5	7.68	24.9	7.83	146.	38.	19.0	2.5	******	40.	19.3	2.40	17.	5.2
12.10	2.	95.00	24.4	12.17	24.8	12.09	579.	220.	1.2	2.8	******	4500.	637.5	2.40	18.	0.1
12.25	3.	97.00	24.8	11.66	25.1	11.63	233.	108.	0.8	2.8	******	116.	1.2	2.40	18.	0.1
12.30	5.	99.00	23.7	11.54	24.1	11.52	176.	80.	0.5	2.5	******	84.	0.8	2.40	18.	0.1
12.40	6.	101.00	23.9	11.34	24.1	11.11	170.	64.	0.3	0.3	******	67.	0.5	2.40	16.	0.1
12.47	10.	103.00	24.5	8.72	24.3	8.77	105.	60.	0.2	0.4	2.10	62.	0.2	2.40	25.	0.1
12.55	11.	105.00	24.1	8.21	25.0	8.15	98.	57.	0.3	0.2	0.80	58.	0.3	2.40	19.	0.1
13.40	14.	107.00	26.1	6.86	26.2	7.12	72.	55.	0.8	0.1	0.58	57.	0.8	2.40	19.	0.1

SET 10

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
13.45	1.	108.00	25.3	7.76	25.9	7.82	146.	37.	19.6	2.8	******	40.	19.3	2.40	21.	5.7
15.30	2.	110.00	25.4	11.78	26.4	11.71	229.	144.	0.8	2.5	******	4063.	593.8	2.40	20.	0.1
15.40	3.	112.00	25.4	11.66	26.0	11.62	276.	140.	1.2	2.5	******	166.	3.5	2.40	20.	0.1
15.48	5.	114.00	24.1	11.53	25.1	11.50	179.	89.	0.3	2.3	******	93.	0.4	2.40	15.	0.1
15.55	6.	116.00	24.2	11.37	25.2	11.32	135.	66.	0.2	1.1	******	73.	0.3	2.40	21.	0.1
16.00	10.	118.00	24.5	8.68	25.0	8.96	107.	55.	0.2	0.5	3.20	64.	0.3	2.40	20.	0.1
16.10	11.	120.00	24.6	8.22	25.2	8.18	94.	53.	0.2	0.1	1.10	54.	0.2	2.40	20.	0.1

SET 11

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
8.20	1.	123.00	24.0	7.71	23.9	7.83	170.	36.	21.5	4.8	******	34.	20.5	2.40	43.	7.3
8.40	2.	125.00	23.8	11.38	23.8	11.35	198.	61.	5.8	3.6	******	176.	23.2	2.40	17.	0.1
8.58	3.	127.00	23.8	11.51	24.0	11.51	192.	72.	0.6	3.2	******	79.	0.6	2.40	17.	0.1
9.17	5.	129.00	23.0	11.47	23.6	11.44	155.	65.	0.3	1.6	******	69.	0.4	2.40	25.	0.1
9.35	6.	131.00	20.8	11.23	22.0	11.19	88.	47.	0.4	0.1	******	49.	0.6	2.40	20.	0.1
9.55	10.	133.00	20.2	8.23	22.3	8.21	88.	46.	0.3	0.1	1.20	48.	0.3	2.40	17.	0.1
10.15	11.	135.00	20.8	7.78	22.6	7.84	87.	46.	0.3	0.1	0.43	47.	0.6	2.40	21.	0.1
10.40	14.	137.00	22.8	7.17	23.7	7.51	85.	48.	0.8	0.1	0.26	49.	0.6	2.40	25.	0.1

SET 12

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
11.10	1.	142.00	24.9	7.64	25.5	7.87	164.	32.	20.2	5.9	******	34.	20.7	2.40	25.	6.8
12.12	2.	144.00	24.6	11.00	25.8	11.03	177.	49.	11.5	3.0	******	184.	22.0	2.40	18.	0.1
11.49	3.	146.00	25.0	11.51	25.0	11.49	192.	73.	0.9	3.4	******	77.	1.3	2.40	20.	0.1
12.34	5.	148.00	24.4	11.42	25.5	11.42	153.	66.	0.8	1.0	******	59.	0.2	2.40	20.	0.1
12.55	6.	150.00	20.8	11.22	23.6	11.08	96.	42.	0.4	0.1	******	49.	0.4	2.40	23.	0.1
13.40	10.	152.00	21.1	7.56	24.2	7.71	85.	46.	0.3	0.1	1.10	45.	0.4	2.40	35.	0.1
13.50	11.	154.00	21.2	7.46	23.8	7.61	87.	46.	0.3	0.1	0.53	47.	0.3	2.40	16.	0.1
14.00	14.	156.00	22.7	6.96	24.2	7.23	78.	44.	0.5	0.1	0.25	47.	0.6	2.40	14.	0.1

SET 13

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
14.05	1.	158.00	25.1	7.66	25.5	7.77	159.	30.	19.4	3.3	******	31.	19.4	2.40	22.	6.3
14.15	2.	160.00	25.4	11.70	25.4	11.66	341.	138.	1.0	3.2	******	300.	21.7	2.40	12.	5.6
14.25	3.	162.00	25.7	11.36	26.4	11.29	176.	82.	0.4	3.0	******	90.	1.0	2.40	16.	0.1
14.35	5.	164.00	24.5	11.34	25.4	11.29	153.	82.	0.3	1.9	******	87.	0.4	2.40	13.	0.1
14.40	6.	166.00	20.4	11.15	23.3	11.06	85.	55.	0.3	0.3	******	60.	0.3	2.40	17.	0.1
14.50	10.	168.00	20.9	7.76	23.0	7.72	86.	56.	0.3	0.6	0.88	60.	0.4	2.40	20.	0.1
15.00	11.	170.00	20.1	7.47	23.1	7.66	96.	56.	0.4	0.1	0.46	60.	0.4	2.40	15.	0.1
15.15	14.	172.00	22.7	6.87	24.2	7.09	72.	55.	0.6	0.1	0.27	60.	0.6	2.40	28.	0.1

SET 14

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
15.20	1.	174.00	25.0	7.68	25.2	7.80	161.	37.	18.4	3.6	******	42.	18.9	2.40	21.	6.6
15.30	2.	176.00	25.1	11.37	25.2	11.38	225.	85.	5.0	3.1	******	228.	20.5	2.40	12.	5.6
15.35	3.	178.00	25.2	11.40	25.2	11.38	173.	79.	1.1	3.0	******	87.	1.1	2.40	16.	0.1
15.45	5.	180.00	23.8	11.40	24.3	11.37	151.	79.	0.3	2.5	******	81.	0.6	2.40	17.	0.1
15.50	6.	182.00	19.5	11.19	22.4	11.07	92.	51.	0.2	0.1	******	56.	0.4	2.40	13.	0.1

SET 15

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
8.25	1.	187.00	23.2	7.78	23.6	7.93	174.	39.	20.2	6.0	******	41.	20.2	2.40	28.	6.9
8.44	2.	189.00	23.3	11.73	22.7	11.74	290.	118.	1.9	4.2	******	272.	21.7	2.40	20.	0.1
9.07	3.	191.00	23.1	11.31	22.6	11.28	125.	66.	0.8	3.6	******	73.	1.2	2.40	20.	0.1
9.25	5.	193.00	22.0	11.33	22.3	11.31	118.	60.	0.4	3.1	******	65.	0.6	2.40	20.	0.1
9.35	6.	195.00	19.0	11.01	20.4	10.94	63.	45.	0.3	0.1	******	48.	0.6	2.40	24.	0.1
9.54	10.	197.00	19.4	7.93	20.7	7.98	65.	44.	0.8	0.1	0.88	47.	0.7	2.40	20.	0.1
10.13	11.	199.00	19.0	7.71	20.4	7.74	63.	44.	0.4	0.1	0.43	46.	0.4	2.40	29.	0.1
10.26	14.	201.00	18.8	7.43	20.4	7.58	58.	52.	5.0	0.1	0.20	46.	0.9	2.40	22.	0.1

SET 16

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
10.43	1.	203.00	22.6	7.63	22.4	7.78	148.	41.	19.8	5.5	******	40.	19.9	2.40	31.	6.4
10.58	2.	205.00	23.2	11.05	22.9	11.02	202.	59.	12.7	3.3	******	169.	21.4	2.40	22.	0.1
11.13	3.	207.00	22.6	11.29	22.8	11.28	126.	60.	4.6	2.4	******	58.	0.8	2.40	22.	0.1
11.27	5.	209.00	21.9	11.33	22.2	11.31	119.	63.	0.3	1.8	******	67.	0.8	2.40	24.	0.1
11.41	6.	211.00	19.0	11.04	20.5	10.93	61.	39.	0.2	0.1	******	44.	0.3	2.40	21.	0.1
11.59	10.	213.00	1.9	28.06	20.5	8.04	61.	45.	0.3	0.1	1.20	47.	0.7	2.40	22.	0.1
12.17	11.	215.00	19.4	7.79	20.3	7.81	61.	43.	0.6	0.3	0.45	51.	4.2	2.40	20.	0.1
12.34	14.	217.00	20.0	7.13	20.6	7.36	58.	42.	0.8	0.1	0.24	42.	0.8	2.40	19.	0.1

SET 17

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
13.30	1.	219.00	23.6	7.64	23.0	7.40	150.	35.	18.4	7.6	******	40.	18.0	2.40	34.	6.0
13.47	2.	221.00	23.0	11.36	22.7	11.37	216.	73.	8.0	5.2	******	212.	20.1	2.40	24.	5.2
14.04	3.	223.00	23.2	11.21	23.3	11.18	118.	53.	1.3	4.0	******	79.	4.0	2.40	22.	0.1
14.21	5.	225.00	22.4	11.27	22.8	11.23	112.	60.	0.7	2.0	******	63.	0.7	2.40	23.	0.1
14.35	6.	227.00	18.8	10.94	20.9	10.89	57.	43.	0.4	0.1	******	46.	0.5	2.40	25.	0.1
14.48	10.	229.00	19.1	8.10	20.7	7.93	58.	44.	0.5	0.1	0.35	45.	0.6	2.40	15.	0.1
15.05	11.	231.00	19.5	7.74	20.8	7.83	57.	46.	0.7	0.1	0.48	45.	0.4	2.40	24.	0.1
15.23	14.	233.00	20.4	7.17	20.3	7.34	57.	43.	0.7	0.1	0.18	44.	0.7	2.40	20.	0.1

SET 18

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
8.25	1.	238.00	22.6	7.58	21.7	7.74	166.	39.	19.5	7.5	******	41.	19.2	2.40	36.	6.3
8.32	2.	240.00	22.5	11.50	21.8	11.43	232.	83.	6.3	5.3	******	212.	21.2	2.40	21.	0.1
8.40	3.	242.00	22.4	10.98	21.4	10.97	130.	47.	4.3	5.7	******	59.	5.2	2.40	27.	0.1
8.50	5.	244.00	21.2	11.02	21.0	10.92	84.	40.	1.8	3.2	******	42.	2.0	2.40	24.	0.1
8.55	6.	246.00	18.1	10.35	19.5	10.27	52.	28.	1.3	0.1	******	30.	1.4	2.40	23.	0.1
9.05	10.	248.00	18.1	0.0	19.2	7.23	37.	30.	1.3	0.1	1.20	30.	1.4	2.40	24.	0.1
9.11	11.	250.00	17.8	7.32	18.8	7.44	39.	29.	1.3	0.1	0.36	31.	1.3	2.40	21.	0.1
9.20	14.	252.00	17.9	7.22	19.0	7.34	45.	31.	0.3	0.1	0.29	32.	0.8	2.40	18.	0.1

SET 19

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
9.27	1.	254.00	22.3	7.60	21.4	7.76	165.	35.	18.4	7.7	******	37.	18.5	2.40	33.	6.0
9.35	2.	256.00	22.4	11.41	21.6	11.33	224.	64.	8.8	5.2	******	168.	19.8	2.40	20.	5.2
9.43	3.	258.00	22.5	10.97	21.7	10.94	128.	44.	4.1	5.3	******	44.	4.6	2.40	24.	0.1
9.50	5.	260.00	21.3	10.98	21.0	10.95	81.	33.	1.7	4.2	******	37.	2.1	2.40	24.	0.1
9.55	6.	262.00	18.2	10.34	19.4	10.26	40.	25.	1.3	0.1	******	26.	1.7	2.40	25.	0.1
10.25	10.	264.00	18.4	7.78	19.6	7.78	38.	29.	1.3	0.1	1.70	28.	1.7	2.40	27.	0.1
10.30	11.	266.00	18.5	7.43	19.5	7.60	39.	29.	1.4	0.1	0.75	29.	1.5	2.40	23.	0.1
10.50	14.	268.00	18.1	7.05	19.3	7.18	41.	31.	0.8	0.1	0.33	29.	0.8	2.40	20.	0.1

SET 20

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
11.00	1.	270.00	22.3	7.97	21.5	8.09	180.	42.	22.7	5.3	******	83.	20.0	2.40	28.	5.0
11.15	2.	272.00	22.2	11.20	22.5	11.15	197.	49.	12.6	5.0	******	160.	22.4	2.40	24.	0.1
11.28	3.	274.00	22.0	10.92	22.4	10.88	130.	43.	4.7	5.2	******	43.	4.7	2.40	23.	0.1
11.40	5.	276.00	21.2	10.91	22.0	10.86	80.	32.	1.8	3.4	******	34.	2.0	2.40	25.	0.1
11.53	6.	278.00	19.0	10.25	20.3	10.18	35.	26.	1.4	0.1	******	26.	1.7	2.40	24.	0.1
12.04	10.	280.00	19.2	8.23	20.7	8.02	35.	27.	1.5	0.1	2.00	30.	1.8	2.40	24.	0.1
12.17	11.	282.00	19.6	7.89	20.8	7.83	37.	29.	1.4	0.1	0.85	32.	1.9	2.40	20.	0.1
12.32	14.	284.00	20.3	7.09	21.2	7.27	40.	33.	1.1	0.1	0.42	33.	1.3	2.40	16.	0.1

SET 21

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
13.13	1.	286.00	23.2	7.63	23.3	7.79	158.	35.	17.0	5.8	******	37.	16.8	2.40	28.	5.3
13.20	2.	288.00	22.9	11.25	23.2	11.23	210.	64.	11.0	4.0	******	184.	18.7	2.40	20.	4.8
13.33	3.	290.00	23.0	10.85	22.8	10.80	130.	50.	5.3	4.3	******	54.	5.7	2.40	22.	0.1
13.48	5.	292.00	22.4	10.86	22.8	10.76	77.	35.	2.1	3.7	******	40.	2.4	2.40	20.	0.1
14.03	6.	294.00	20.2	10.11	22.0	9.98	34.	27.	1.6	0.1	******	30.	1.7	2.40	21.	0.1
14.15	10.	296.00	21.2	7.57	22.4	7.72	35.	28.	1.6	0.1	1.20	29.	1.8	2.40	20.	0.1
14.30	11.	298.00	21.4	7.76	22.2	7.51	37.	27.	1.6	0.1	0.46	30.	1.6	2.40	20.	0.1
14.45	14.	300.00	21.0	7.18	22.0	7.36	40.	32.	0.9	0.1	0.27	32.	0.9	2.40	18.	0.1

SET 22

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
8.08	1.	305.00	22.2	7.75	21.6	7.89	169.	41.	16.8	6.2	******	38.	16.0	2.40	19.	5.0
8.20	2.	307.00	22.3	11.28	22.4	11.29	222.	64.	8.5	4.7	******	168.	16.6	2.40	19.	0.1
8.31	3.	309.00	22.4	10.92	22.4	10.88	132.	50.	3.6	4.7	******	55.	3.7	2.40	38.	0.1
8.40	5.	311.00	21.4	10.41	21.7	10.29	60.	28.	2.6	3.0	******	30.	2.9	2.40	22.	0.1
8.51	6.	313.00	18.3	9.48	20.0	9.39	33.	24.	2.5	0.2	******	26.	2.6	2.40	23.	0.1

SET 23

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
9.02	1.	315.00	22.4	7.68	21.8	7.87	165.	37.	15.7	6.0	******	35.	15.5	2.40	26.	4.8
9.12	2.	317.00	22.8	11.34	22.4	11.32	214.	62.	7.5	5.4	******	176.	16.8	2.40	19.	4.4
9.22	3.	319.00	22.8	10.93	22.4	10.88	130.	44.	3.3	4.9	******	49.	3.7	2.40	22.	0.1
9.33	5.	321.00	22.0	10.37	21.8	10.27	65.	26.	2.6	3.1	******	29.	2.8	2.40	21.	0.1
9.42	6.	323.00	19.0	9.44	20.2	9.37	32.	23.	2.5	0.1	******	26.	3.2	2.40	23.	0.1

SET 24

TIME	SP	SN	T(R)	PHR	T(F)	PHF	TA	CAF	MGF	NH3	TURB	CAT	MGT	FLOW	COD	PO4-P
0.0	14.	31.00	24.7	6.81	25.5	6.96	44.	39.	1.4	0.1	******	*****	*****	2.40	20.	0.1
0.0	14.	32.00	24.7	6.69	25.6	7.04	48.	36.	1.4	0.1	******	*****	*****	2.40	15.	0.1
0.0	14.	184.00	25.4	7.15	25.6	7.42	83.	52.	0.8	0.1	******	*****	*****	2.40	19.	0.1
0.0	14.	185.00	25.5	7.21	26.4	7.55	87.	61.	0.9	0.1	******	*****	*****	2.40	16.	0.1
0.0	14.	186.00	25.4	7.03	26.4	7.22	70.	57.	0.8	0.1	******	*****	*****	2.40	13.	0.1
0.0	14.	235.00	22.6	7.29	22.8	7.47	84.	57.	0.7	0.1	******	*****	*****	2.40	13.	0.1
0.0	14.	236.00	22.5	7.25	22.3	7.44	77.	55.	0.6	0.1	******	*****	*****	2.40	17.	0.1
0.0	14.	237.00	22.8	7.08	23.1	7.20	71.	57.	0.8	0.1	******	*****	*****	2.40	13.	0.1
0.0	14.	302.00	23.2	7.52	23.0	7.66	68.	49.	0.5	0.1	******	*****	*****	2.40	16.	0.1
0.0	14.	303.00	23.2	7.14	23.0	7.38	58.	42.	0.4	0.1	******	*****	*****	2.40	16.	0.1
0.0	14.	304.00	22.7	7.16	22.8	7.52	55.	42.	0.4	0.1	******	*****	*****	2.40	20.	0.1
0.0	14.	325.00	22.2	7.18	21.7	7.23	42.	29.	0.7	0.1	******	*****	*****	2.40	20.	0.1
0.0	14.	326.00	22.0	7.10	21.8	7.20	40.	37.	0.8	0.1	******	*****	*****	2.40	20.	0.1
0.0	14.	327.00	22.0	7.14	21.6	7.24	38.	32.	0.8	0.1	******	*****	*****	2.40	16.	0.1
0.0	14.	328.00	22.0	7.15	22.2	7.27	37.	31.	1.0	0.1	******	*****	*****	2.40	17.	0.1

APPENDIX 17

ANALYTICAL METHODS *

All the analytical methods used in this investigation were taken from "Standard Methods for the Examination of Water and Wastewater" by the APHA-AWWA-WPCF, 14th Ed., 1975 and "Theoretical Aspects and Analytical Methods - Analytical Guide, Part II" published by National Institute for Water Research, CSIR (1975). The principles of the methods used are indicated below, for further details the reader is refered to the above two references.

MANUAL METHODS

Alkalinity

Potentiometric tritration with standard sulphuric acid to a pH end point (*Standard Methods*, pp 278 - 282).

Hardness (calcium, magnesium and total)

EDTA titrimetric method (*Standard Methods*, pp. 202 - 206)

Nitrogen (Kjeldahl)

Total Kjeldahl nitrogen (ammonia and organic nitrogen) is determined as follows. In the presence of sulphuric acid, potassium sulphate and mercuric sulphate catalyst, the amino nitrogen of many organic materials is converted to ammonium sulphate. After the mercury ammonium complex in the digestate has been decomposed by sodium thiosulphate, the ammonia is distilled from an alkaline medium and absorbed in boric acid. The ammonia is determined by titration with a standard mineral acid (*Standard Methods*, pp 437 - 440).

Oxygen Demand (Chemical)

A sample is refluxed with known amounts of potasium dichromate and sulphuric acid and the excess dichromate is titrated with ferrous

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* See Chapter 2 to 7, subsections on Methods

ammonium sulphate (*Standard Methods*, pp 550-554).

pH Value

pH values are determined by means of a combined or separate glass and calomel electrodes and an electronic pH meter (*Standard Methods*, pp. 460-465).

Solids (suspended, total, total dissolved)

Suspended solids were determined by filtering off the suspended material from a suitable volume of sample. The membrane filter technique was used.

Total solids were determined by evaporating to dryness a known volume of sample, and drying and weighing the residue.

Total dissolved solids were determined by filtering a sample through Whatman No. 42 filter paper. A known volume of filtrate was evaporated, dried and weighed (All three methods are given in the *Analytical Guide*, pp 171-181).

Turbidity

Nephelometric method - The method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions (*Standard Methods*, pp. 132-134).

ATOMIC ABSORPTION

Atomic absorption methods were used for the determination of all metals in solution, i.e. calcium, magnesium, potassium and sodium (*Analytical Guide*, pp. 76 - 88).

AUTOMATED METHODS - AUTO ANALYZER

Chloride

Ferricyanide method (*Analytical Guide*, pp. 10 - 11).

Nitrogen - Ammonia

Nitroprusside method (*Analytical Guide*, pp. 23 - 24).

Nitrogen - Nitrate

Rhenium - stannous chloride - diacetyl monoxime method (*Analytical Guide*, pp. 32 - 33)

Oxygen Demand (Chemical)

Digestion with potassium dichromate and sulphuric acid (*Analytical Guide*, pp. 35-36).

Phosphorus (Ortho)

Ammonium molybdate method (*Analytical Guide*, pp. 41-42).

Phosphorus (Total)

The sample is digested with sulphuric and perchloric acids. The various phosphate forms are hydrolyzed to ortho-phosphate, which is then determined by the ammonium molybdate method (*Analytical Guide*, pp. 26-29).

Sulphate

Barium chloride method (Analytical Guide, p. 46).

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APPENDIX 18

$CaCO_3$ SOLID PHASE CHARACTERIZATION*

The solid phase plays a significant role in the $CaCO_3$ precipitation process. The rate of crystallization is reported to be proportional to the 'active surface area'. In addition, separation of the crystals from the liquid phase is a function of the crystals' particle size distribution and shape.

A study was made of the following physical characteristics of $CaCO_3$ crystals, sludges and scales,

(1) Appearance,
(2) Crystallographic form,
(3) Specific surface area, and
(4) Particle size distribution.

Methods

The following calcium carbonate samples were collected for study,

(1) MERCK brand analytical reagent grade calcium carbonate,
(2) HOPKIN and WILLIAMS brand analytical reagent grade calcium carbonate,
(3) BRITISH DRUG HOUSE (BDH) brand analytical reagent grade calcium carbonate,
(4) Sludge formed in the SWRP** lime reactor,
(5) Scale deposited on bench-scale pilot plant reactor walls during lime treatment of secondary effluent,
(6) Sludge formed in the SWRP equalization pond,
(7) Scale deposited on SWRP ammonia stripping tower slats,
(8) Scale deposited on SWRP recarbonator walls,
(9) Sludge formed in the SWR pilot plant recarbonator,

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* See Chapter 2, p. 29 and Chapter 3, p. 137

** SWRP - Stander Water Reclamation Plant

(10) Scale deposited on bench-scale pilot plant reactor walls, during calcium carbonate precipitation from pure solutions of $CaCl_2$, $NaHCO_3$ and NaOH.

The samples were oven dried (110°C), cooled to ambient temperature and ground to a powder using a mortar and pestle. The samples were then distributed to the service departments of a number of CSIR Institutes (NPRI, CERG, NIBR) where the four analyses were undertaken on each $CaCO_3$ sample,

Appearance was studied by optical and electron microscopy.

Crystallographic form was determined by powder X-ray spectroscopy.

Specific surface area was determined by nitrogen adsorption measurements on a Ströhlein area meter.

Particle Size Distribution was determined by seive analysis and sedimentation techniques.

RESULTS

The results of these various determinations are summarized in Table A18.1. Electron microscope microphotographs and optical microscope microphotographs are shown in Figures A18.1 to A18.3. Particle size distributions are listed in Table A18.2 and are illustrated in Figures A18.4 and A18.5.

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TABLE A18.1

PHYSICAL PROPERTIES OF VARIOUS $CaCO_3$ SAMPLES

ORIGIN	PHYSICAL APPEARANCE	CRYSTALLOGRAPIC FORM	SPECIFIC SURFACE AREA	50% MASS MEDIAN DIAMETER
			m^2/g	um
MERCK BRAND - CRYSTALS	Rhombohedrons	Calcite	0,70	4,6
HOPKIN & WILLIAMS BRAND - CRYSTALS	Rhombohedrons	Calcite	0,51	10
BRITISH DRUG HOUSE BRAND - CRYSTALS	Rhombohedrons	Calcite	0,56	-
LIME REACTOR - SWRP - SLUDGE	Flaky	Calcite and traces of Magnecite	1,29	-
LIME REACTOR - BPP - SCALE	Flaky	Calcite and traces of Dolomite	-	7,5-90
EQUALIZATION POND - SWRP - SLUDGE	Globular Particles	-	4,43	230
AMMONIA STRIPPING TOWER - SWRP - SCALE	Crystalline Particles	-	33,6	33,6
RECARBONATOR - SWRP - SCALE	Crystalline Particles	-	2,89	-
RECARBONATOR - SWRP - SLUDGE	Rhombohedrons	Calcite	-	13
REACTOR - BPP - PURE $CaCO_3$ SCALE	Rhombohedrons and Rosettes	Calcite ($\pm$ 90%) and Vaterite ($\pm$ 10%)	-	20-25

* BPP - Bench-scale pilot plant

Figure A18.1. Electron microscope - microphotographs

1. MERCK brand calcium carbonate (X3000); 2. SLUDGE from SWRP primary clarifier (X1600); 3. SCALE from SWRP ammonia stripping tower slats (X1000); 4. SCALE from SWRP recarbonation reactor walls (X2800)

1.

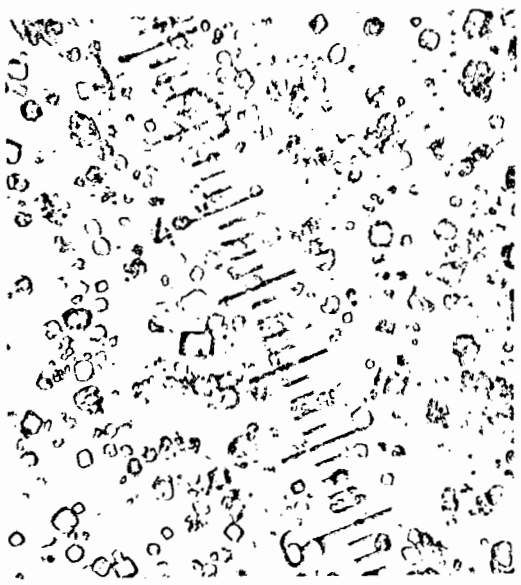
2.

3.

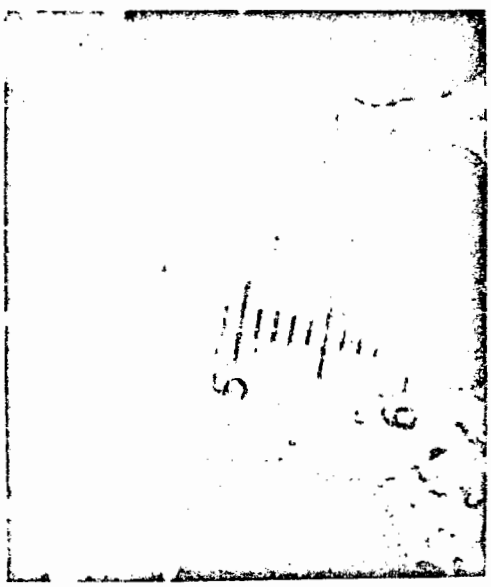
4.

Figure A18.2. Optical microscope - microphotographs

1. Sludge from pilot plant recarbonator (X360); 2. Sludge from SWRP equilization pond (X96).



1.



2.

IDENTIFICATION OF MICROPHOTOGRAPHS ON NEXT PLATE

SAMPLES 1 & 2 : $CaCO_3$ scale from reactor wall bench-scale experiment with pure $CaCl_2$, NaOH and $NaHCO_3$ (x360).

SAMPLES 3 & 4 : $CaCO_3$ scale from reactor wall, bench-scale experiment with lime and humus tank effluent (X360).

SAMPLE 5 : Merck brand calcium carbonate (X360)

SAMPLE 6 : Hopkin and Williams brand calcium carbonate (X360)

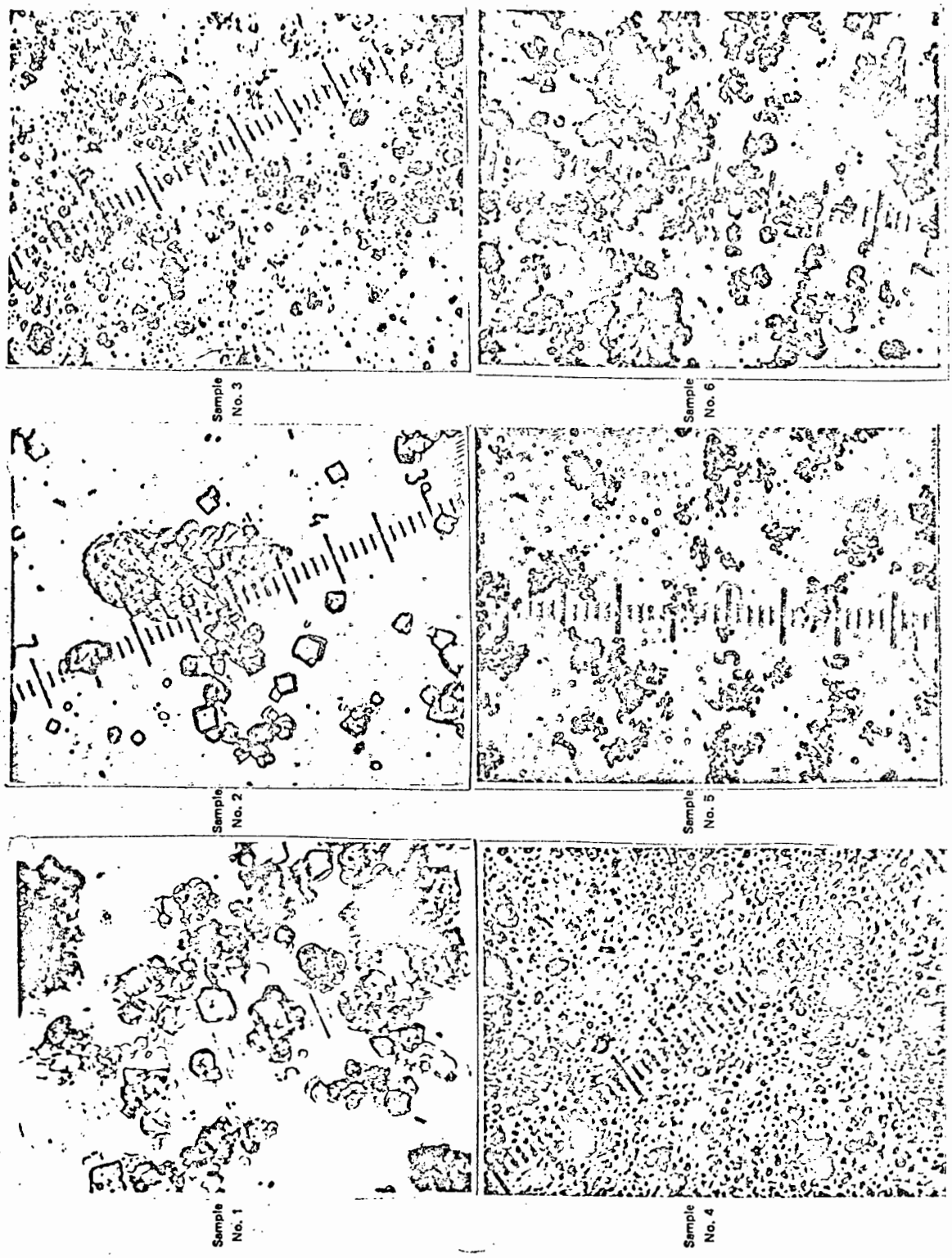


Figure A18.3. Microphotographs of 6 calcite samples - Magnification = 360X

Table A18.2

Particle size distributions of six calcite samples

Particle size (equivalent Stokes diameter) µm	Sample No.*					
	1	2	3	4	5	6
	% Finer than size					
60		99				
50	100	95,5		100		
40	97	87	100	98,5		
30	86	70	98	96,5	99,5	
25	72	55	94	94	97,5	100
20	51	40	87	92	95,5	98
15	28,5	24	71	82	92,5	84
12	19	15,5	60,5	72	88,5	61
10	14	11	53,5	63,5	84	40
8	11	7	45	54	79	22
6	7,5	2	32	40	68	12
5	-	0,5	25,5	33	57	10
4	5	-	17,5	25	35	8
3	-	-	10,5	17	13	5
2	-	-	4,5	10	1	3
1,5	3	-	2,5	6,5	-	2
1	-	-	0,5	4	-	-
0,8	-	-	-	2,5	-	-

*Sample identification is given on p A18.6

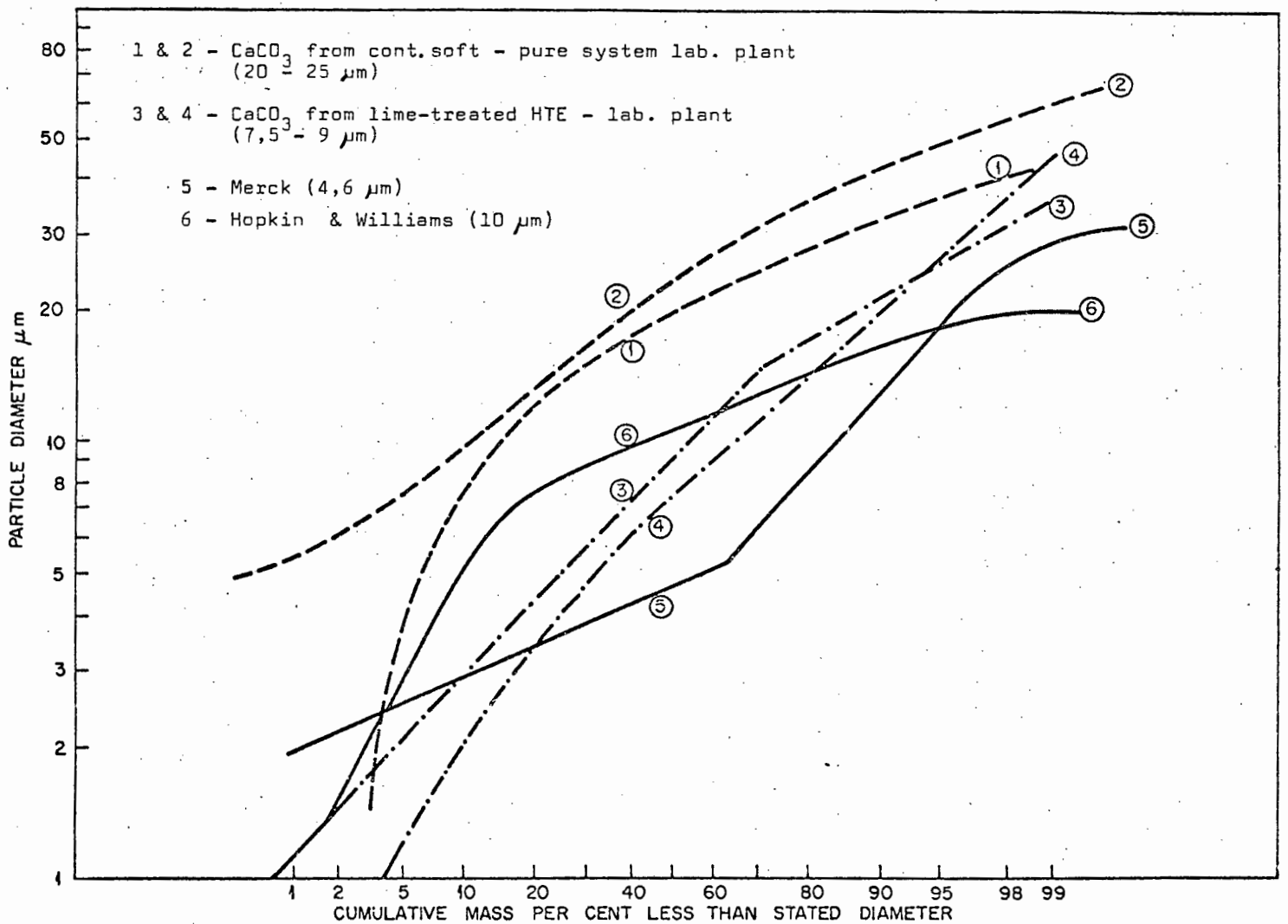


Figure A18.4. Particle size distribution of six types of calcite samples

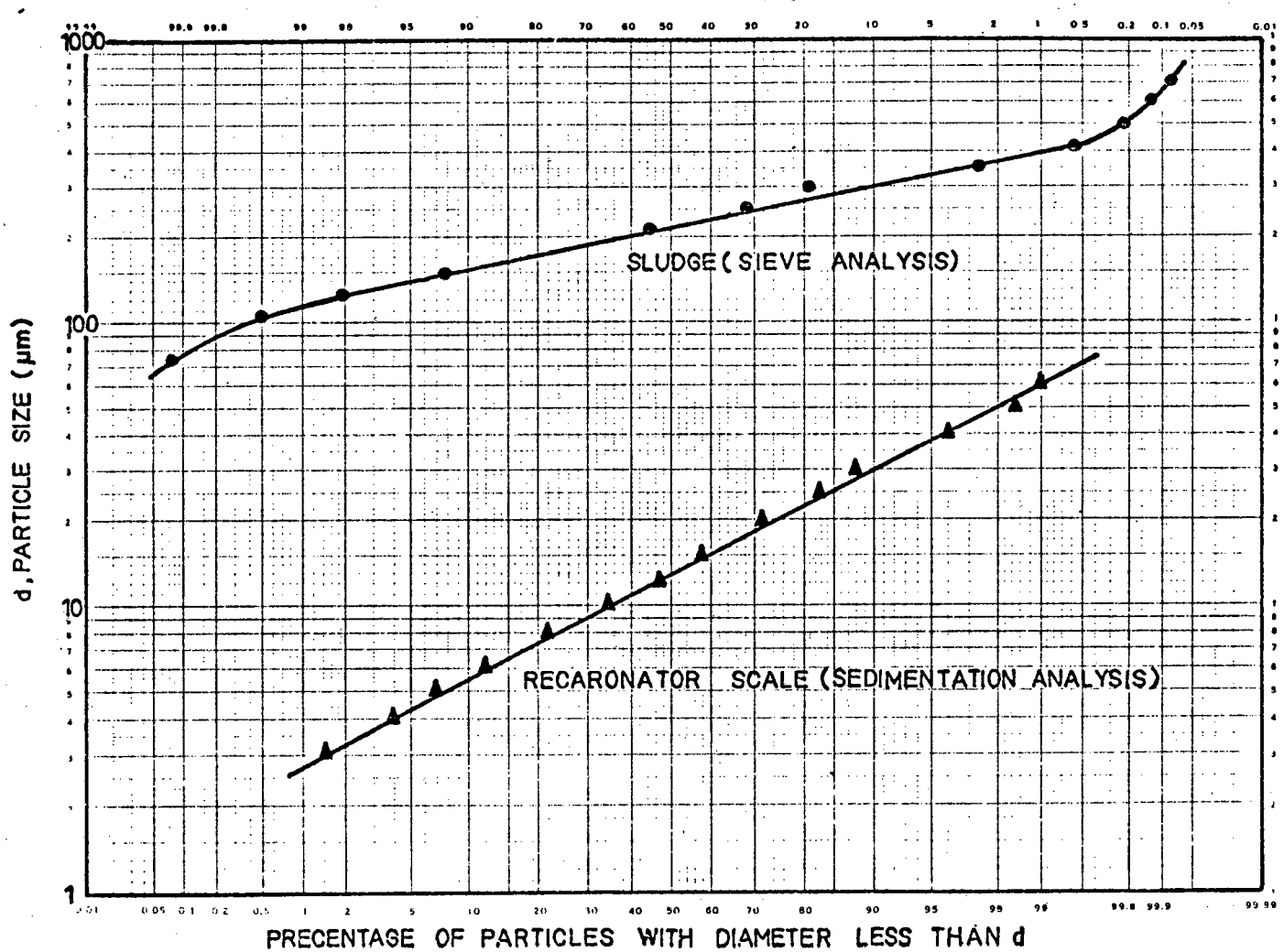


Figure 18.5. Partical size distribution of lime sludge and pulverized recarbonator scale

APPENDIX 19

PUBLICATIONS

Two publications on work dealt with in this thesis have been published in the open literature,

(1) "Calcium Carbonate Crystallization Kinetics"
by H N S Wiechers, P Sturrock and G v R Marais,
Water Research 9, pp. 835-845 (1975).

(2) "Calcium Carbonate and Magnesium Hydroxide Solubility Product Values for Heterogeneous Systems" by H N S Wiechers.
This paper was presented at the 8th International Conference of the IAWPR, in Sydney, Australia, 17-22nd Oct., 1976. It was subsequently published in Prog. Wat. Tech. 9, pp. 531-545 (1977).

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Water Research Vol. 9, pp. 835 to 845. Pergamon Press 1975. Printed in Great Britain.

CALCIUM CARBONATE CRYSTALLIZATION KINETICS*

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(*Received* 30 *August* 1974)

Abstract—The kinetics of crystallization of calcium carbonate were studied by following changes in pH only on batch solutions of $CaCl_2$, $NaHCO_3$ and NaOH in the presence of calcite seed crystals. The Ca^{+2} and CO_3^{-2} concentrations were derived by taking account of the equilibrium relationships between the species of the carbonic—and calcium systems with changes in pH and ionic strength. Reactant concentrations and seed crystal masses studied were in the same range as that found in water softening practice. At these high concentrations the crystallization kinetics continued to conform to the crystallization model of Reddy and Nancollas. Removal of Ca^{+2} from solution follows a rate equation first order with respect to Ca^{+2} and CO_3^{-2} concentrations, the activation energy for crystal growth is $10{\cdot}3 \pm 0{\cdot}9$ kcal mol^{-1} and the rate is independent of the stirring speed, all suggesting a surface controlled process. The rate constant is a function of the pH established immediately after mixing of the reactants. The rate of Ca^{+2} removal from solution is directly proportional to the mass of crystals present in the reaction solution. Numerical integration of the rate equation gives a solution for the design of calcium carbonate crystallization reactors.

INTRODUCTION

Calcium and magnesium ions are the most common metals associated with hardness in water. They are present in varying concentrations in virtually all natural waters but are particularly evident in underground and surface waters derived from dolomitic areas and often in effluents from domestic and industrial areas. The principle underlying the removal of Ca^{+2} and Mg^{+2} ions is to induce the formation of CO_3^{-2} and OH^- ions. The solubility products $[Ca^{+2}]\cdot[CO_3^{-2}]$ and $[Mg^{+2}]\cdot[OH^-]^2$ are low and if exceeded, $CaCO_3$ and $Mg(OH)_2$ respectively, crystallize out.

Chemical dosing for the removal of these ions has been essentially solved by the development of methods based on equilibrium chemistry of the carbonic system, by Caldwell and Lawrence (1953), and Loewenthal and Marais (1973). However, chemical reactions in the softening process are time dependent, in particular the rate of crystallization of $CaCO_3$ can be slow—in many processes as designed, there is insufficient time for the reaction to go to completion (AWWA, 1951). In a large measure the insufficient time allowed for complete crystallization in these processes is as a result of a lack of understanding of the kinetics of the crystallization of $CaCO_3$ and $Mg(OH)_2$ out of solution. Consequences of insufficient crystallization are "after precipitation", encrustation of the sand particles in the sand filters and "lime" deposits in the pipes of the water reticulation system.

The importance of water softening processes, and especially the "excess" lime process and the economic consequences attendant on their use, makes it imperative that the kinetics of the crystallization phenomena be thoroughly investigated. This paper deals with the crystallization kinetics of calcium carbonate from synthetically prepared supersaturated calcium carbonate solutions.

Crystallization can be categorized into two processes, i.e. nucleation and growth. Nucleation is the generation ("birth") of crystals from solution. Growth is the process whereby solute is transported to the crystal surface and is then oriented into the crystal lattice. In water softening processes both nucleation and growth processes may be operative. Growth is the dominant process if the precipitant or crystal concentration is high and is referred to as heterogeneous crystallization. When there are no or only small concentrations of crystals present both nucleation and growth takes place simultaneously, and is referred to as spontaneous or homogenous crystallization.

Spontaneous crystallization of calcium carbonate from supersaturated solutions has been studied by a number of investigators (Brooks, Clark and Thurston, 1950; Gruzensky, 1966; Kitano and Hood, 1965; Reitemeier and Buehrer, 1940). However, the spontaneous crystallization process does not permit reliable kinetic analysis to be made since the implied assumption that homogeneous nucleation takes place is of doubtful validity (Nancollas and Purdie, 1968): nucleation is likely to occur on impurity particles which offer available sites for crystal growth, and during spontaneous crystallization both the total number and size distribution of the particles vary.

Reddy and Nancollas (1971a,b) have reported on the kinetics of crystallization of calcium carbonate

* Portions of this work to be submitted towards the partial fulfilment of a higher degree by H. N. S. Wiechers, at the University of Cape Town.

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in the presence of inoculant seed crystals. They followed the reaction by observing changes in the calcium and hydrogen ion concentrations. The studies were made under conditions of slight supersaturation and in a pH range of 8·4–8·8. They found that Ca^{2+} removal from solution follows a rate equation first order with respect to the concentrations of Ca^{+2} and CO_3^{-2}, that the activation energy is relatively high, 11·0 kcal mol^{-1} and that the crystallization rate is independent of the stirring speed. These three observations all suggest a surface controlled crystallization process.

The present study is concerned with the kinetics of calcium carbonate precipitation under typical water softening-practice conditions, i.e. high degree of oversaturation, moderately high concentration of seed mass, and a pH range of 8–10. The technique of calcite seed inoculation, suggested by Reddy and Nancollas (1971a,b) was used in this investigation as it is more reliable than the spontaneous crystallization technique.

CALCIUM CARBONATE CRYSTALLIZATION THEORY

The following three sets of equilibrium relationships must be taken into account in solutions from which calcium carbonate precipitates:

(1) Carbonic species and water equilibria

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \quad (1)$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \quad K_1 \quad (2)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{-2} \quad K_2 \quad (3)$$

$$H^+ + OH^- \rightleftarrows H_2O \quad K_w \quad (4)$$

(2) Ion-pair equilibria

$$Ca^{+2} + HCO_3^- \rightleftarrows CaHCO_3^+ \quad K_{CaHCO_3^+} \quad (5)$$

$$Ca^{+2} + CO_3^{-2} \rightleftarrows CaCO_3^0 \quad K_{CaCO_3^0} \quad (6)$$

$$Ca^{+2} + OH^- \rightleftarrows CaOH^+ \quad K_{CaOH^+} \quad (7)$$

(3) Solid-Liquid-Phase equilibrium

$$Ca^{+2} + CO_3^{-2} \rightleftarrows CaCO_3(S) \quad K_{sp} \quad (8)$$

The K values above are taken as the thermodynamic equilibrium constants for the carbonic and calcium systems in pure water, i.e.

$$pK_1 = 17052/TA + 215{\cdot}21 \log(TA) - 0{\cdot}12675(TA) - 545{\cdot}56$$
(Harned and Davis, 1943)

$$pK_2 = 2902{\cdot}39/TA + 0{\cdot}02379(TA) - 6{\cdot}498$$
(Harned and Scholes, 1943)

$$pK_w = 4787{\cdot}3/TA + 7{\cdot}1321 \log(TA) + 0{\cdot}01037(TA) - 22{\cdot}801$$
(Harned and Hamer, 1933)

$$pK_{sp} = 0{\cdot}01183(TS) + 8{\cdot}03$$
(Langmuir, 1968)

$$pK_{CaCO_3^0} = -3{\cdot}200 - 684{\cdot}886(1/TA + 1/298{\cdot}15)$$
(Truesdell and Jones, 1973)

$$pK_{CaHCO_3^+} = -1{\cdot}260 - 1385{\cdot}309(1/TA - 1/298{\cdot}15)$$
(Truesdell and Jones, 1973)

$$pK_{CaOH^+} = -1{\cdot}299 - 260{\cdot}388(1/TA - 1/298{\cdot}15)$$
(Truesdell and Jones, 1973)

Where

TS = Temperature (°C)
TA = Temperature (°K)
$pK = -\log K$

Using mass action concepts the relations between the K values and the species concentrations are as follows:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} \cdot f_M^2 = K_1 \quad (9)$$

$$\frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} \cdot f_D = K_2 \quad (10)$$

$$[H^+][OH^-] \cdot f_M^2 = K_w \quad (11)$$

$$\frac{[Ca^{+2}][HCO_3^-]}{[CaHCO_3^+]} \cdot f_D = K_{CaHCO_3^+} \quad (12)$$

$$\frac{[Ca^{+2}][CO_3^{-2}]}{[CaCO_3^0]} \cdot f_D^2 = K_{CaCO_3^0} \quad (13)$$

$$\frac{[Ca^{+2}][OH^-]}{[CaOH^+]} \cdot f_D = K_{CaOH^+} \quad (14)$$

$$[Ca^{+2}][CO_3^{-2}] \cdot f_D^2 = K_{sp} \quad (15)$$

and

$$pH = -\log([H^+] \cdot f_M) \quad (16)$$

where

[] = designates concentration in mol l^{-1}
f_M = activity factor for monovalent ions
f_D = activity factor for divalent ions

The activity factors are calculated from the Davies (1967) equation.

For the monovalent ion:

$$-\log f_M = 0{\cdot}51 \times 1 \times 1 \times \left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0{\cdot}30 \times I\right]$$

i.e. $-\log f_M = 0{\cdot}51 \times F(I)$ (17)

For the divalent ion:

$$-\log f_D = 2{\cdot}04 \times F(I)$$

where

$$I = 0{\cdot}5 \Sigma Z_i^2 C_i \quad (19)$$

I = Ionic strength of solution
Z_i = Ionic charge of the i^{th} ion in solution
C_i = Molar concentration of the i^{th} ion in solution

To establish equations of state the following assumptions are made.

(1) On mixing solutions containing carbonic and calcium species the ionic equilibria described by equations (2–7) are attained very rapidly and the reactions can be taken as complete within milliseconds. For calculation purposes the attainment of these equilibria is assumed to be instantaneous.

(2) Equilibrium state for precipitation as described by equation (8) is attained slowly, i.e. the rate of calcium carbonate crystallization is relatively slow as compared to the rate of attainment of ionic equilibrium. The crystallization is therefore time dependent.

(3) At the maximum ionic strength envisaged in this investigation (<0·01) Na^+ and Cl^- form negligible ion-pairs with other ions. For this reason supersaturated solutions of $CaCO_3$ were constituted by mixing solutions of $NaHCO_3$, $CaCl_2$ and NaOH. Ion-pairing effects of Na^+ and Cl^- were not incorporated into the solution.

(4) In the pH range 8 to 10 and at calcium and carbonic species concentrations $0{\cdot}5 \times 10^{-3}$ to $2{\cdot}0 \times 10^{-3}$ mol l^{-1} (which is the range of concentrations investigated in this paper), the concentration of the ion-pair $CaOH^+$ is relatively low compared to the concentrations of Ca^{+2}, $CaCO_3^0$ and $CaHCO_3^+$ and can be neglected.

The following example illustrates the above statement: consider the following solution near the upper pH limit:

Total calcium = $1{\cdot}223 \times 10^{-3}$ mol l^{-1}

Total carbonic species = $1{\cdot}540 \times 10^{-3}$ mol l^{-1}

pH of solution = 9·87

Using the thermodynamic dissociation constants: K_{CaCO_3}, $K_{CaHCO_3^+}$ and K_{CaOH^+}, the concentrations of the various calcium species can be calculated.

Ion	Concentration (mol l^{-1})	Ratio w.r.t. to $CaOH^+$
Ca^{+2}	$9{\cdot}43 \times 10^{-4}$	628·7
$CaCO_3^0$	$2{\cdot}84 \times 10^{-4}$	189·3
$CaHCO_3^+$	$1{\cdot}14 \times 10^{-5}$	7·6
$CaOH^+$	$1{\cdot}50 \times 10^{-6}$	1·0

Ratio $CaOH^+$/Total free and paired Ca ions = 1/826·6. At lower pH values the ratio will be even smaller.

Initial supersaturated ionic state

The initial state is defined as the *ionic* state of the solution, when equilibrium has been established, immediately after the chemicals have been mixed but before crystallization has commenced. This ionic state is described by Equations (9–13), (17–19) and the following four equations ($CaOH^+$ is neglected):

(1) Equation for electro-neutrality

$$[CaHCO_3^+] + [Na^+] + [H^+] + 2[Ca^{+2}] = [OH^-] + 2[CO_3^{-2}] + [HCO_3^-] + [Cl^-] \quad (20)$$

(2) Equation for total carbonic species

$$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] + [CaCO_3^0] + [CaHCO_3^+] \quad (21)$$

(3) Equation for ionic strength

$$I = 0{\cdot}5([H^+] + [Na^+] + 4[Ca^{+2}] + [OH^-] + 4[CO_3^{-2}] + [HCO_3^-] + [Cl^-] + [CaHCO_3^+]). \quad (22)$$

(4) Equation for total calcium species in solution

$$T_{Ca} = [Ca^{+2}] + [CaCO_3^0] + [CaHCO_3^+]. \quad (23)$$

The above 12 equations contain 21 variables:

C_T; $[Na^+]$; $[Ca^{+2}]$; T_{Ca}; $[Cl^-]$; $[H_2CO_3]$; $[HCO_3^-]$; $[CO_3^{-2}]$; $[CaCO_3^0]$; $[CaHCO_3^+]$; $[H^+]$; $[OH^-]$; K_1; K_2; K_w; $K_{CaCO_3^0}$; $K_{CaHCO_3^+}$; $F(I)$; I; f_D; f_M.

However, there are nine known parameters, i.e.

C_T; $[Na^+]$; $[Cl^-]$; T_{Ca}; K_1; K_2; K_w; $K_{CaCO_3^0}$; $K_{CaHCO_3^+}$

and 12 independent equations, equations (9–13) and (17–23). Thus there are 21 variables with 21 known values or independent relationships. Hence, it is theoretically possible to calculate all the unknown species concentrations and the pH at the initial equilibrium state of the reaction solution, i.e. at $t = 0$.

Since the ionic strength is a function of the concentration of the ionic species and vice versa, an iterative calculation procedure must be used to simultaneously determine both the species concentrations and the ionic strength (Davies, 1967). In this investigation the calculations were made by means of a digital computer program, EXPDAT. (Program EXPDAT is available on request. The effect of ion-pairing due to such ions as SO_4^{-2} has not been included and waters containing such ions should not be analysed using the program.)

Crystallization state

Subsequent to the establishment of the initial ionic state, calcium carbonate crystallization from solution commences. Neglecting the ion-pair $CaOH^+$ in the pH range below 10 (assumption 4) the change in total calcium concentration, T_{Ca}, due to crystallization must equal the change in total carbonic species in solution, C_T, as equal moles of calcium and carbonates are removed during crystallization of calcium carbonate, i.e.

$$\Delta T_{Ca} = \Delta C_T \quad (24)$$

Due to ion pairing effects the change in Ca^{+2} ions is not equal to the change in C_T. This can be shown as follows:

$$\Delta T_{Ca} = T_{Cai} - T_{Ca} = ([Ca^{+2}]_i + [CaHCO_3^+]_i + [CaCO_3^0]_i) - ([Ca^{+2}] + [CaHCO_3^+] + [CaCO_3^0]) = \Delta[CaCO_3(S)] \quad (25)$$

$$\Delta C_T = C_{Ti} - C_T = ([H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{-2}]_i + [CaHCO_3^+]_i + [CaCO_3^0]_i) - ([H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] + [CaHCO_3^+] + [CaCO_3^0]) \quad (26)$$

where

$[]_i$ designate initial concentrations at time, $t = 0$ (mol l^{-1}).

$[]$ designate concentrations at time, $t = t$ (mol l^{-1}).

From equation (26) substitute ΔC_T for ΔT_{Ca} in equation (25) and solve for ΔCa^{+2}, i.e. $[Ca^{+2}] - [Ca^{+2}]$

$$\Delta Ca^{+2} = [Ca^{+2}]_i - [Ca^{+2}] = ([H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{-2}]) - ([H_2CO_3] + [HCO_3^-] + [CO_3^{-2}]) \quad (27)$$

At any time, t, during the crystallization period the state of the reaction solution is described by equations (9–12), (16–23) and (27).

These equations contain 25 variables:

$[H_2CO_3]_i$; $[HCO_3^-]_i$; $[CO_3^{-2}]_i$; $[Ca^{+2}]_i$; $[H_2CO_3]$; $[HCO_3^-]$; $[CO_3^{-2}]$; $[Ca^{+2}]$; $[H^+]$; $[OH^-]$; $[CaCO_3^0]$; $[CaHCO_3^+]$; $[Na^+]$; $[Cl^-]$; K_1; K_2; K_w; $K_{CaCO_3^0}$; $K_{CaHCO_3^+}$; pH; $F(I)$; I; f_M; f_D; T_{Ca}.

However, there are the following known parameters:

(1) Six initial ionic equilibrium concentrations at time zero ($t = 0$) available from previous calculation: $[H_2CO_3]_i$; $[HCO_3^-]_i$; $[CO_3^{-2}]_i$; $[Ca^{+2}]_i$; $[Na^+]$ and $[Cl^-]$.

(2) Five equilibrium constants: K_1; K_2; K_w; $K_{CaCO_3^0}$ and $K_{CaHCO_3^+}$.

(3) Thirteen equations of state: equations (9–12), (16–23) and (27).

There are therefore 25 variables with 24 values or independent relationships and hence only one variable needs to be measured. The variable most convenient and simplest to measure is pH. Thus by measuring the pH the system is completely defined and can be solved, i.e. all the ion species concentrations with the exception of $CaOH^+$ can be calculated for any measured pH value knowing only the initial reactant concentrations, equilibrium constants and the equations of state.

Knowing the initial ionic state and the ionic state at the measured pH, the concentration of $CaCO_3(S)$ precipitated is calculated from equation (25). (These calculations were made by means of computer program EXPDAT). Thus the time behaviour of calcium carbonate crystallization can now be studied by monitoring only the pH with time.

If all the species concentrations including the ion-pair $CaOH^+$ are to be calculated, two parameters have to be measured experimentally. The necessity for this is shown as follows: from equation (24) the change in total calcium due to $CaCO_3$ precipitation is equal to the change in the carbonic species, hence equation (27). As we have seen this allows all the species in solution to be determined except $CaOH^+$. If $CaOH^+$ is to be determined equation (14) replaces equation (27) and equations (20), (22) and (23) are modified to incorporate ($CaOH^+$). A number of variables cancel but the number of parameters to be measured increases by two. The system to be solved now consists of:

(1) Thirteen equations: equations (9–12), (14) and (16–23). (2) Eight constants: K_1; K_2; K_w; $K_{CaCO_3^0}$; $K_{CaHCO_3^+}$; K_{CaOH^+}; $[Na^+]$; $[Cl^-]$. (3) Two measured variables: i.e. say T_{Ca} and pH.

Measurement of T_{Ca} and pH was the approach used by Reddy and Nancollas (1971a,b). However, measurement of T_{Ca} enormously increases the difficulty of experimental investigations. Where high rates of crystallization are encountered, as in this investigation it is indeed doubtful if accurate measurements of T_{Ca} are possible. (Reddy and Nancollas investigated crystallization in conditions where the rate was very slow.) The great advantage in measuring only pH is that no back-up analytical work is required. It is therefore of great practical value to delineate the region in which pH measurement suffices to define the system.

The important question which must be resolved is how reliable is the pH measurement. One cannot utilize pH measurement if the rate of reaction is so fast that the response of the glass electrode is insufficient to reflect the true pH change. Mattock (1954) has reviewed the literature on the feasibility of using glass electrodes to measure relatively fast changes in pH values. One concludes from his review that the response of the glass electrode is sufficiently rapid to monitor relatively fast $CaCO_3$ crystallization rates.

CALCIUM CARBONATE CRYSTALLIZATION KINETICS

The analysis so far was only concerned with the determination of the ionic state and crystal mass precipitated at any particular moment when the pH is measured, but it gives no indication of how the state changes with time. However, monitoring pH with time, and using the theory set out above, the time behaviour of all the species, particularly Ca^{+2}, CO_3^{-2}, $CaCO_3(S)$ (i.e. crystal mass) and f_D can be calculated.

Reddy and Nancollas (1971a,b) proposed the following model for change in Ca^{+2} concentration with time:

$$\frac{d[Ca^{+2}]}{dt} = -K \cdot S \cdot ([Ca^{+2}] \cdot [CO_3^{-2}] - K_{sp}/f_D^2) \quad (28)$$

where

$[Ca^{+2}]$ = molar concentration of Ca^{+2} ions (mol l^{-1})

$[CO_3^{-2}]$ = molar concentration of CO_3^{-2} ions (mol l^{-1})

K = rate constant for calcite crystallization (l mol^{-1} min^{-1})/(mg seed l^{-1})

S = total surface area of seed crystals

K_{sp} = solubility product for $CaCO_3$ (mol^2 l^2)

f_D^2 = activity factor for divalent ions

Having the calculated values of Ca^{+2}, CO_3^{-2}, $CaCO_3(S)$ and f_D with time, one may test the validity of equation (28). Reddy and Nancollas (1971a,b) established the validity of this equation for Ca^{+2} concentrations in the range $1{\cdot}40 \times 10^{-4}$–$4{\cdot}44 \times 10^{-4}$ mol l^{-1} (14·0–44·4 mg l^{-1} as $CaCO_3$); and CO_3^{-2} concentrations in the range $1{\cdot}83 \times 10^{-4}$–$3{\cdot}79 \times 10^{-4}$ mol l^{-1} (18·3–37·9 mg l^{-1} as $CaCO_3$). These ranges

of concentration give rise to relatively slow calcium removal rates, about 1×10^{-6}–10×10^{-6} mol l^{-1} min^{-1}, and ion-pairing effects are minimal.

Concentrations of calcium and carbonate ions encountered in practice in softening, "excess" lime and recarbonation processes often are greater than the concentrations studied by Reddy and Nancollas (1971a, b), by one or more orders of magnitude, and up to 25 per cent of the total calcium concentration may be in the $CaCO_3^0$ ion-pair form (Wiechers, 1973). Furthermore, concentrations, size distribution and total area of solid $CaCO_3$ available for crystal growth may also deviate considerably from those studied. Consequently, one should not apply rate equation (28) in these circumstances without prior investigation to determine whether it is still applicable.

Reddy and Nancollas (1971a,b) found that the rate of Ca^{+2} removal from solution is directly proportional to the inoculant seed mass. They could therefore replace S, the surface area factor in equation (28) by M, the concentration of inoculant seed crystals. However, when the concentration of $CaCO_3$ crystallizing out is significant relative to the inoculant crystal concentration this relationship can be only approximately true since the total available surface area may change significantly, not only due to increase in mass but also due to change in surface to mass ratio. Therefore in this study it was endeavoured to established if it is possible to replace S by the total calcium carbonate crystal concentration $[CaCO_3(S)]$, present in the reactor at any time, t, and if the rate constant, K, now linked to $CaCO_3(S)$ is affected by concentration of $CaCO_3(S)$.

MATERIALS AND METHODS

Analytical reagent grade chemicals were used throughout. MERCK brand $CaCO_3$ seed crystals were used for all experiments unless indicated otherwise. Carbon dioxide free distilled water, with a conductivity less that 5 μ S, was used throughout. Stock solutions (0·01 M) of sodium bicarbonate, sodium hydroxide and calcium chloride were made up and standardized before each series of tests. Borax was used as a primary standard and sulphuric acid as a secondary standard against which the sodium hydroxide and bicarbonate stock solutions were standardized, using a method of endpoint determination as set out by Loewenthal and Marais (1973). The calcium stock solutions were standardized by the EDTA method (Standard Methods, 1971).

A batch reactor was designed to have minimal air-solution contact to prevent carbon dioxide adsorption or desorption (Fig. 1).

The reactants were made up in two 250 ml volumetric flasks, one containing the $NaHCO_3$-NaOH solution, the other the $CaCl_2$ solution. These were poured into the two reactant solution cylinders and on opening the valve discharged through the mixing block to the reactor where the pH change with time was measured. In later experiments it was found preferable to first discharge the solution containing the carbonic species and subsequently the solution containing the calcium species. Mixing intensity was adequate and the pH was already at a high value when the $CaCl_2$ solution was received.

The solution was stirred by means of a teflon-coated magnetic stirring bar. The temperature in the reactor and waterbath was kept constant (± 0·1°C) by means of a thermostat (HAAKE E52). The pH changes accompanying calcium carbonate precipitation were followed using a Radiometer pH meter (Type PHM 26c) with Radiometer glass and calomel electrodes and recorded continuously on a Hewlett Packard strip chart recorder (Type 7100B. Amplifier Type 17501A). Borax and phosphate NBS standard buffers, in the pH range of interest, were used to calibrate the electrode system.

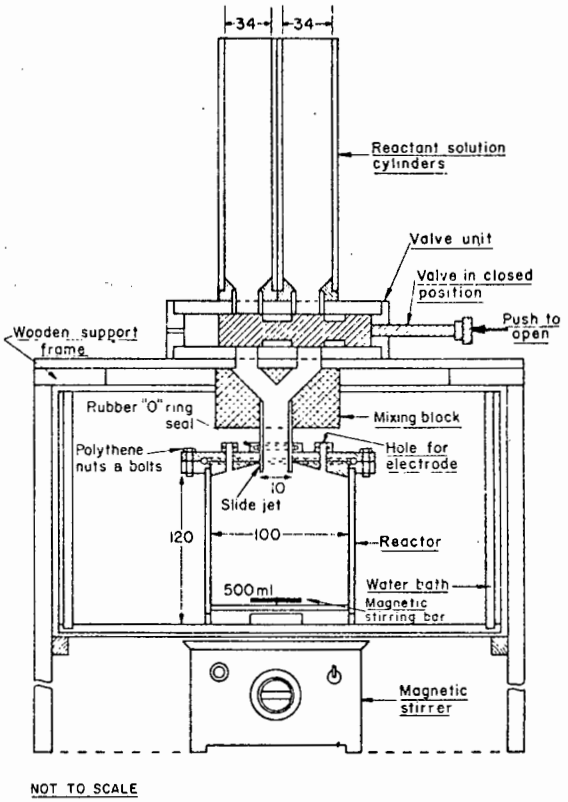

Fig. 1. Front elevation of water bath, supporting frame and reactor vessel.

RESULTS AND DISCUSSION

Examples of pH-time curves for some experiments on calcium carbonate crystallization from solution are given in Fig. 2. From the initial reactant concentrations and the observed pH change with time, the following time dependent parameters were calculated from equations (9–12), (16–23) and (27), using the computer program EXPDAT:

$$[H^+];[OH^-];[CaHCO_3^+];[CaCO_3^0];[CaCO_3(S)];$$

$$[H_2CO_3];[HCO_3^-];[CO_3^{-2}];f_M \text{ and } f_D.$$

A plot of some of the derived values for exp. 35H is shown in Fig. 3. To determine K in equation (28), the derived values $[Ca^{+2}]$, $[CO_3^{-2}]$, $[CaCO_3(S)]$ and f_D were plotted according to $\Delta[Ca^{+2}]/\Delta t$ vs $[CaCO_3(S)] \times ([Ca^{+2}] \times [CO_3^{-2}] - K_{sp}/f_D^2)$. Theoretically if K is constant in an experiment the data should plot to a straight line, as is evident in Fig. 4. This plot therefore verifies the crystallization model of Reddy and Nancollas (1971a,b).

Once it was established that the Reddy and Nancollas model is valid, an investigation was instituted to determine the factors influencing the value

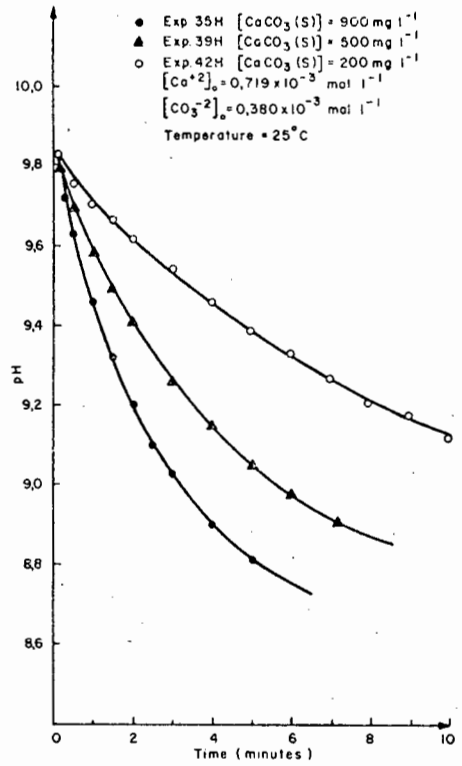

Fig. 2. Experimentally measured pH variation with time, for various $CaCO_3$ seed crystal concentrations.

of K. This involves investigation of four aspects: the effect of (1) various seed concentrations for constant initial reactant concentrations; (2) constant seed concentration and various initial reactant concentrations; (3) temperature, and (4) stirring speed.

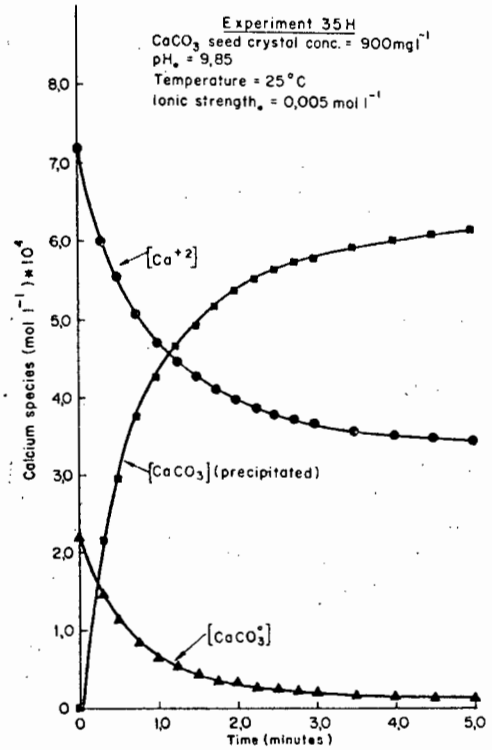

Fig. 3. Plot of derived calcium species versus time, from experimentally measured pH-values.

(1) Constant reactant concentration of $[Ca^{+2}]_0$ and $[CO_3^{-2}]_0$ of $0{\cdot}719 \times 10^{-3}$ and $0{\cdot}380 \times 10^{-3}$ mol l^{-1} respectively was inoculated with crystal seed masses ranging from 100 to 1000 mg l^{-1}. The stirring speed was kept constant at 500 rev min^{-1} and the temperature at 25°C. The results are listed in Table 1. The value of K remained constant over this range of crystal seed mass at $K = 2{\cdot}1 \pm 0{\cdot}2$ (l mol^{-1} min^{-1})/(mg seed l^{-1}). At seed crystal concentrations less than 400 mg l^{-1} an initial surge in growth rate was observed (Fig. 5) with subsequent time-crystallization behaviour according to equation (28) and the value of K unchanged. The initial growth surge can be attributed to the formation of new nuclei under conditions where insufficient area or growth sites are supplied by the inoculated crystals.

(2) In this series the seed crystal mass was kept constant at 700 mg l^{-1} and $CaCl_2$, $NaHCO_3$ and NaOH concentrations varied over a wide spectrum of molarities, as listed in Table 2 where the derived data are also given. Again the stirring speed and temperature were kept constant at 500 rev min^{-1} and 25°C respectively. It is evident that the initial concentration influences the rate constant (see Fig. 6) and it would appear that the K value can be related to the initial ionic equilibrium pH value, pH_0. A plot of pH_0 versus K is shown in Fig. 7 for MERCK and Hopkins and Williams brand crystals.

Considering the series of experiments under (1) and (2) together it is clear that the value of K is dependent only on the initial pH_0 value and that in the course of a crystallization experiment this K value is unaffected by the reduction in pH (see Fig. 6). If (in the course of the experiment) the K value is influenced by pH then at the same pH the slopes of the experimental plots reported in Fig. 6 should have been the same, whereas this was not observed. No satisfactory hypothesis can be advanced for this observed behaviour.

(3) To study the effect of temperature on K the same initial reactant concentrations were used, and crystallization was monitored at temperatures 10, 20, 30 and 40°C. At each temperature the seed mass was varied from 400 to 800 mg l^{-1}. The measured variation of K with temperature includes the effect of pH_0, since pH_0 is a function of temperature. The results are recorded in Table 3 (see Fig. 8). To determine the functional relationship of K with temperature the Arrhenius plot, ln K vs $1\ T^{-1}$ was made, as shown in Fig. 9, from which it appears that the Arrhenius equation

$$\ln K = \ln A - E R T^{-1} \qquad (29)$$

adequately describes the temperature dependence of K. The values of ln A and E were calculated by applying a linear least squares fit to the data-points in Fig. 9 to give:

$$\ln A = 18{\cdot}0\ (\pm\ 1{\cdot}5)$$

$$E = 10{\cdot}3\ (\pm\ 0{\cdot}9)\ \text{kcal mol}^{-1}$$

An activation energy of this magnitude indicates that

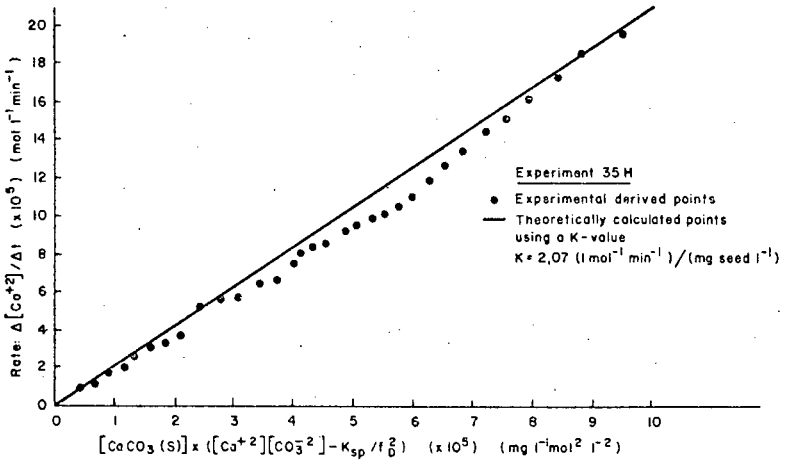

Fig. 4. Graph indicating the linearity of the plot of rate versus function $[CaCO_3(S)] \times ([Ca^{+2}][CO_3^{-2}] - K_{sp}/f_D^2)$.

Table 1. Rate constant for various seed crystal concentrations

Experiment No.	Seed crystal concentration (mg l^{-1})	Rate constant K (litre·mol^{-1} min^{-1}) (mg seed·litre^{-1})
34H	1000	2·47
35H	900	2·44
36H	800	2·24
37H	700	2·80
38H	600	2·50
39H	500	2·46
40H	400	2·58
41H	300	2·15
42H	200	2·18
43H	100	2·37

$[Ca^{+2}]_0 = 0{\cdot}719 \times 10^{-3}$ mol l^{-1}.
$[CO_3^{-2}]_0 = 0{\cdot}380 \times 10^{-3}$ mol l^{-1}.
Stirring speed 500 rev min^{-1}.
Temperature = 25°C.

the reaction is surface controlled. This value of E is in good agreement with that found by Reddy and Nancollas (1971a, b), i.e. $E = 11{\cdot}0\ (\pm\ 1{\cdot}0)$ kcal mol^{-1}. Thus, even at the fairly high rates of crystallization observed here the crystallization mechanism still appears to be surface controlled.

The Van 't Hoff-Arrhenius equation is widely used by engineers to determine temperature effects, i.e.

$$K_T = K_{20}\theta^{(T-20)} \tag{30}$$

i.e. $\log K_T = \log K_{20} + (T - 20)\log\theta$

where

T = Temperature in °C

K_T, K_{20} = K at temperature T°C, 20°C respectively

θ = Constant.

To determine if the K values obtained in this investigation obey equation (30) a plot was made of $\log K_T$ vs T°C. The plot approximates to a straight line, yielding:

$$K_T = 1{\cdot}53 \times 1{\cdot}053^{(T-20)} \tag{31}$$

(4) To determine the effect of the stirring speed on the rate constant, K, stirring speeds were investigated ranging from 300 to 800 rev min^{-1} (see Table 4). A minimum stirring speed of 400 rev min^{-1} appeared necessary to keep the crystals in suspension in the reactor. Stirring speeds higher than this value did not perceptibly change the rate constant. Independence of K from the stirring speeds lends further support to a surface controlled mechanism for crystallization (Reddy and Nancollas, 1971a, b).

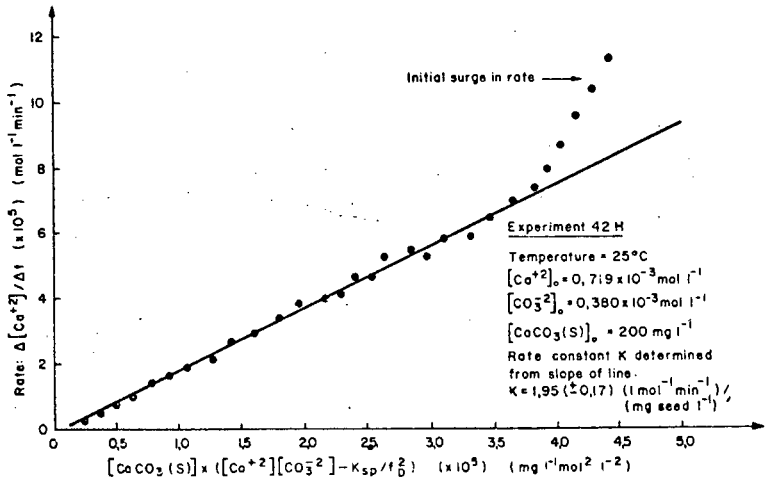

Fig. 5. Plot indicating initial surge in rate of calcium ion removal when inoculated seed mass was low.

Table 2. Rate constant at various reactant concentrations and various initial pH values

Experiment No.	$CaCl_2$ $\times 10^3$	$NaHCO_3$ $\times 10^3$	NaOH $\times 10^3$	$[Ca^{+2}]_0$ $\times 10^3$	$[CO_3^{-2}]_0$ $\times 10^3$	pH_0 ($t = 0$)	Rate constant
40	3·720	3·480	1·310	2·838	0·453	9·51	1·11
41	3·720	3·078	1·210	2·862	0·379	9·52	1·12
43	3·720	2·305	0·906	3·087	0·287	9·50	1·03
44	3·720	1·920	0·756	3·187	0·232	9·49	0·98
45	3·720	1·535	0·605	3·291	0·179	9·47	0·98
46	2·790	3·460	1·320	2·001	0·539	9·59	1·35
47	2·790	3·078	1·210	2·054	0·486	9·64	1·37
48	2·790	2·790	1·060	2·136	0·401	9·64	1·40
49	2·790	2·305	0·906	2·225	0·335	9·63	1·30
50	2·790	1·920	0·756	2·311	0·271	9·57	1·20
54	1·940	2·680	1·060	1·396	0·493	9·69	1·68
55	1·940	2·330	0·906	1·462	0·405	9·67	1·66
56	1·940	1·915	0·756	1·533	0·324	9·65	1·54
57	1·940	1·530	0·605	1·608	0·247	9·63	1·59
62	0·970	1·915	0·756	0·700	0·433	9·78	1·70
63	0·970	1·530	0·605	0·745	0·329	9·77	1·89

Temperature = 25°C; Stirring rate = 500 rev min^{-1}.
$CaCO_3$ seed concentration = 700 mg l^{-1}.

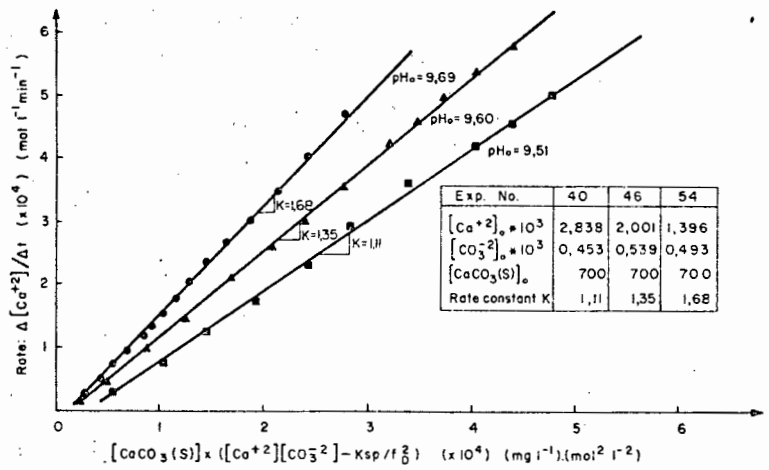

Fig. 6. Effect of initial pH (pH_0) on rate constant K.

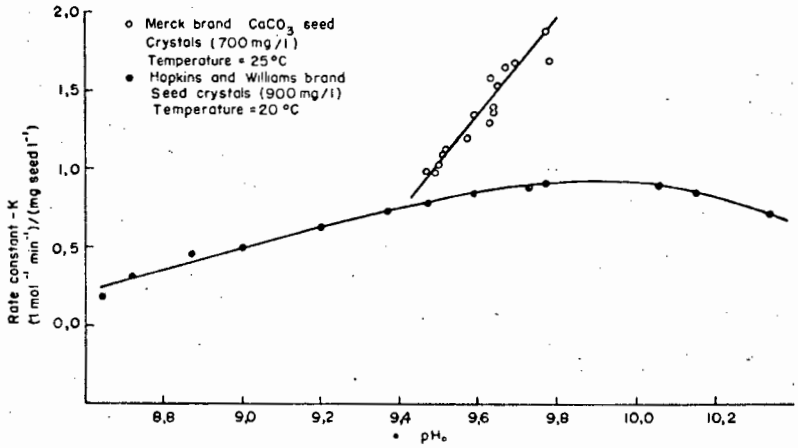

Fig. 7. Plot indicating the relationship between the rate constant and pH_0 for two brands of $CaCO_3$.

Table 3. Rate constant for $CaCO_3$ precipitation at various temperatures

Experiment No.	Crystal seed (mg l^{-1})	Temperature (°C)	Rate constant
1	400	10·6	0·92
2	500	11·0	0·89
3	600	11·4	0·95
4	700	10·6	0·76
5	800	10·8	0·79
6	400	20·8	1·64
7	500	20·5	1·48
8	600	20·4	1·47
9	700	20·8	1·51
10	800	20·8	1·54
11	400	29·0	2·52
12	500	29·1	2·55
13	600	29·0	2·49
14	700	29·1	2·37
15	800	29·0	2·41
16	400	39·8	4·91
17	500	39·7	4·77
18	600	40·0	4·57
19	700	39·0	3·53
20	800	39·0	4·20

Reactant concentrations (mol l^{-1}): $CaCl_2 = 1{\cdot}19 \times 10^{-3}$; $NaHCO_3 = 1{\cdot}56 \times 10^{-3}$; $NaOH = 0{\cdot}69 \times 10^{-3}$; Stirring speed = 500 rev min^{-1}.

APPLICATION

The problem faced by the design engineer is exactly opposite to that in this investigation. In the experimental investigation reactant and crystal seed concentrations are known and the pH change with time is measured. Using this data the change in species concentrations with time, and the rate constant, K, are calculated. In design the chemical quality of the water to be treated is determined experimentally, chemical addition and seed concentration are specified, a value for K is assumed and the time behaviour of the pH and all the species have to be determined. Time behaviour is achieved by numerical integration of equation (28) in conjunction with the ancillary equations for species distribution. A computer program, SOLDIV (available on request) was developed to perform the integration, using values of initial reactant and seed mass concentrations and the experimentally determined rate constant from Exp. 35H. The observed and theoretical values for pH and calcium species versus time are compared in Fig. 10 and the experimentally derived and theoretical kinetic plots in Fig. 11. It would appear that provided a reliable value for K is available, the progress with time of the crystallization process can be closely predicted for any initial reactant concentration and for crystal seed concentration greater than 100 mg l^{-1} in the temperature range 10–40°C.

At this stage caution must be exercised in applying the theory to design:

(1) The theory must still be applied to the completely mixed process with recycling of the sludge. From a theoretical point of view this does not present a difficult problem.

(2) SO_4^{-2} ions have a relatively high ion-pairing potential. In this investigation their presence was deliberately omitted as the objective was to test the crystallization theory with as little interference as possible from other effects such as ion-pairing and ionic strength. However, it is essential that the investigation be extended to incorporate ion-pairing effects of all the ions which may be present in water particularly at higher ionic strengths.

(3) Effects of phosphates and magnesium on crystallization still need to be investigated. Their presence may significantly alter the rate of crystallization and they are always present in waste waters. Organic material may have a further inhibiting effect on crystallization.

(4) A preliminary investigation has indicated that if a different brand crystal seed is used in the crystallization experiments, the rate constant, K, may differ by 100% and possibly more. The value of K appears to depend significantly on the manner in which the crystals are prepared. In practice, pilot scale investiga-

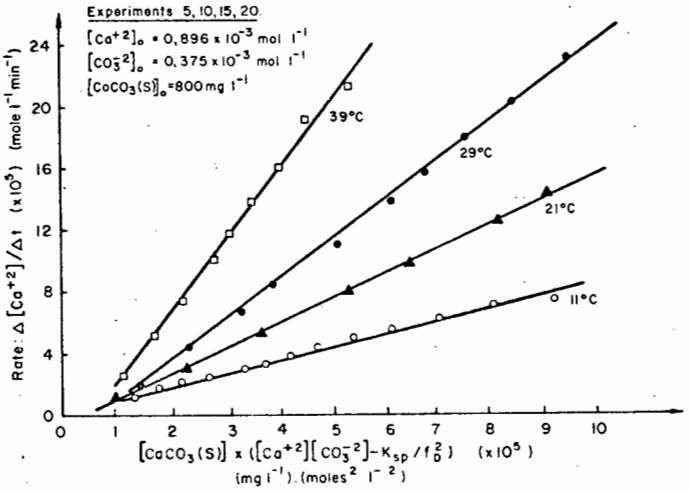

Fig. 8. Effect of temperature on kinetic plots.

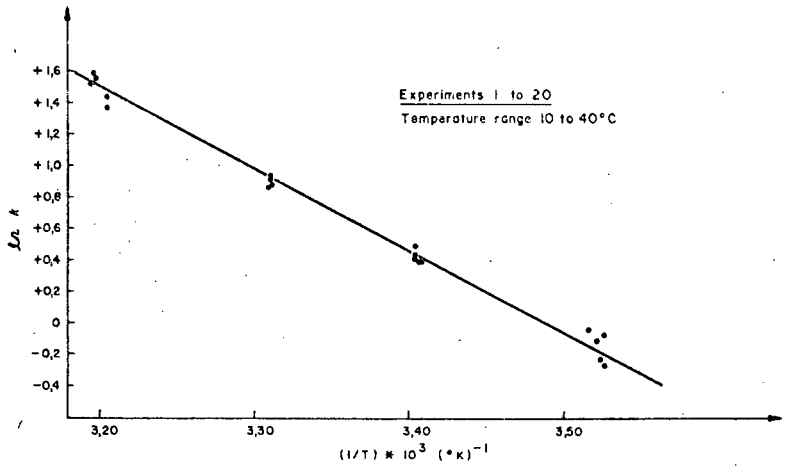

Fig. 9. Graph indicating linearity of Arrhenius plot for heterogeneous $CaCO_3$ precipitation in the temperature range 10–40°C.

Table 4. Rate constant at various stirring rates

Experiment No.	Stirrer rate (rev min^{-1})	Rate constant K ($l\ mol^{-1}\ min^{-1}$)/(mg seed·l^{-1})
30	300	1·46
31	400	1·66
32	500	1·82
33	600	1·94
34	700	1·74
35	800	1·86

Seed concentration = 500 mg l^{-1}, $[Ca^{+2}]_0 = 0{\cdot}72 \times 10^{-3}$ mol·l^{-1}; $[CO_3^{-2}]_0 = 0{\cdot}29 \times 10^{-3}$ mol·l^{-1}; Temperature 21°C.

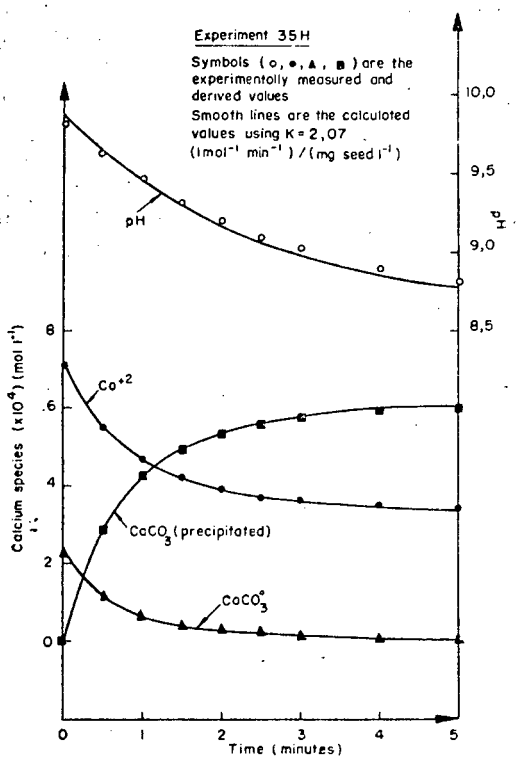

Fig. 10. Graph illustrating both the experimentally measured and derived values, and the calculated values using program SOLDIV.

tions are recommended to determine the crystal characteristics in any particular water softening process.

CONCLUSIONS

(1) When reactants are mixed to give a supersaturated solution of calcium carbonate, the equilibrium state is attained nearly instantaneously, thereafter crystallization commences. The process of crystallization can be monitored by measuring only the pH with time. This procedure is valid provided the pH is below about 10, when the $CaOH^+$ species can be neglected. At higher pH two parameters need to be measured as $CaOH^+$ is no longer negligible.

(2) The crystallization process conforms to the model for Ca^{+2} removal proposed by Reddy and Nancollas (1971a, b), i.e.

$$-\frac{d[Ca^{+2}]}{dt} = K\cdot[CaCO_3(S)]\cdot([Ca^{+2}][CO_3^{-2}] - K_{sp}/f_D^2)$$

where the free ions Ca^{+2} and CO_3^{-2} are calculated taking ion-pairing and activity factors into consideration. $[CaCO_3(S)]$ is the crystal mass at any time, t. The model appears to be valid for Ca^{+2} and CO_3^{-2} concentrations ranging from $1{\cdot}40 \times 10^{-4}$ to $3{\cdot}29 \times 10^{-3}$ mol l^{-1} and $1{\cdot}83 \times 10^{-4}$ to $5{\cdot}29 \times 10^{-4}$ mol l^{-1} respectively, and calcium carbonate seed crystal concentrations ranging from 100 to 1000 mg l^{-1}. These ranges cover those expected in water softening practice.

(3) The removal rate constant, K, is temperature dependent according to the Arrhenius relationship, i.e.

$$K = A\,e^{-E/RT}$$

with E = activation energy = $10{\cdot}3 \pm 0{\cdot}9$ kcal mol^{-1}.

(4) K is independent of the stirring speed and the seed mass concentration, but is dependent on the initial ionic equilibrium pH value, pH_0.

(5) The high activation energy, independence of the

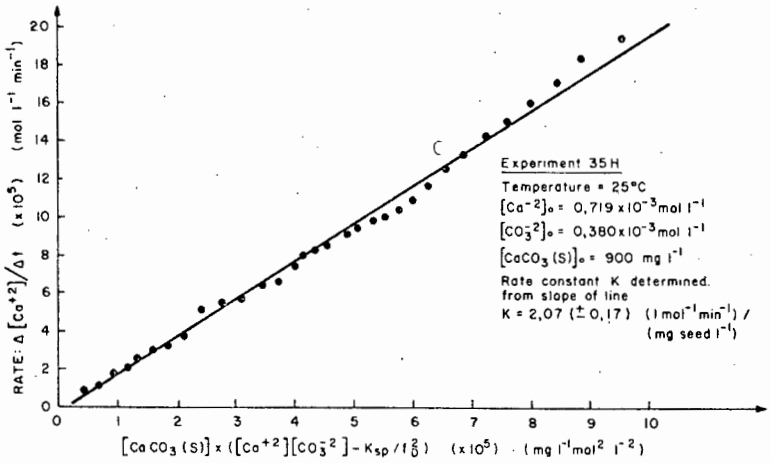

Fig. 11. Comparison between experimentally derived and theoretically calculated kinetic plots.

rate constant of crystallization on stirring speed and the first order dependence of the rate of removal of Ca^{+2} on the concentrations of Ca^{+2} and CO_3^{-2} all support the hypothesis that the crystallization process is surface controlled. Although K is dependent on the total surface area and the available crystallization sites, this investigation shows that the mass of crystals can substitute for the surface area. As the surface to mass ratio will differ between crystals of different origin, the K value cannot yet be determined *ab initio*, but must be determined by experiment.

(6) Knowing only the initial reactant inputs and the seed mass, together with a reliable estimate of the rate constant, K, it is possible to predict the crystallization-time behaviour.

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CALCIUM CARBONATE AND MAGNESIUM HYDROXIDE SOLUBILITY PRODUCT VALUES FOR HETEROGENEOUS SYSTEMS

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SUMMARY

Calcium carbonate and magnesium hydroxide solubility product values were determined for stable lime-treated and recarbonated secondary sewage effluents. Empirical models correlating these solubility product values with the major parameters characterizing the stable effluents were established.

Calcium carbonate and magnesium hydroxide degree of supersaturation were calculated for effluents from various process units of a water reclamation plant. Degree of supersaturation calculations based on experimentally determined solubility product values, agreed significantly better with practical findings than those based on thermodynamic solubility product values.

Solubility product values determined in this study closely agree with those reported in the literature for lime-treated raw sewage and other heterogeneous effluents. Their application is therefore not limited to treated secondary effluents only. In general, for lime-treated sewage effluents, the extent of calcium carbonate and magnesium hydroxide precipitation in reactors, and resultant effluent stability, can now be calculated.

Lime is used in the treatment of effluents (VAN VUUREN *et al.*, 1967) to precipitate phosphates, carbonates and magnesium, and to remove a considerable fraction of the residual soluble, colloidal and suspended organic matter. In a subsequent unit process, carbon dioxide is added to the lime-treated water to precipitate the excess calcium added in the initial unit process. The final water must be stable with respect to the above mentioned precipitants to ensure that no 'after precipitation' takes place. The processes described above give rise to two problems:

(1) What constitutes a stable water, i.e. one that will not give rise to 'after precipitation' (a classical equilibrium problem).

(2) What must the residence time(s) and configuration of the reactor(s) be to ensure a virtually stable water (a kinetic problem involving the rates of precipitation).

Although both these problems are dealt with in the literature, the theoretical and experimental investigations have been oriented principally to synthetic systems. When theoretical models are applied to practice, the

predictions are disappointing. The reasons for this divergence are seldom clear. Furthermore, it is unlikely that it will be possible to delineate and quantify the various factors responsible for the divergent results in the immediate future. In the interim, an empirical approach appears to be the only feasible one. If, as a starting point, the constants derived from the best correlation between experimental and predicted results, are used in the models developed for synthetic systems, more realistic values may be obtained. Such an approach would have even greater value as a predictive tool if the results were applicable to a variety of waters. In any event, the model could be used as a control procedure for the specific water for which it was developed.

The design of precipitation reactors requires solutions of both the equilibrium and kinetic problems. The solution of the equilibrium problem is a prerequisite for the solution of the kinetic problem. In this paper, only the equilibrium problem is considered. The models developed for predicting the solubility products of calcium carbonate and magnesium hydroxide are essentially those proposed for synthetic systems. The constants were derived from data obtained from a water reclamation plant. The systems studied were: stable lime-treated secondary effluent and stable recarbonated effluent.

MODEL DEVELOPMENT

$CaCO_3$ SOLUBILITY PRODUCT

The thermodynamic solubility product for calcium carbonate is defined as:

$$K_{CaCO_3} = (Ca^{2+})(CO_3^{2-}) \quad (1)$$

$$= [Ca^{2+}] \cdot f_{Ca^{2+}} \cdot [Ca^{2+}] \cdot f_{CO_3^{2-}} \quad (2)$$

The most recent estimate of this solubility product at 25 °C is:

$$K_{CaCO_3} = 4{,}01 \times 10^{-9} \text{ mol}^2 \ell^{-2} \quad (pK_{CaCO_3} = 8{,}40 \pm 0{,}02) \text{ (LANGMUIR, 1968).}$$

TRUESDELL and JONES (1973) predicted the temperature dependence of this solubility product from thermodynamic considerations, i.e.

$$pK_{CaCO_3} = 10{,}710 - 698{,}61/T \quad (3)$$

DEDEK (1966) indicated in a literature review of calcium carbonate systems that parameters, other than temperature, influence the solubility of calcium carbonate. Some of these parameters are: magnesium, phosphates, organic matter, ionic strength, particle size and crystallographic type of $CaCO_3$ used. The combined effect of some of these parameters on the $CaCO_3$ solubi-

lity product may be observed when treating wastewaters with lime. MERRILL and JORDEN (1974) presented pK_{CaCO_3}-values for various types of lime-treated effluents (Table 1). Their data show that:

(1) Solubility product values appear to be roughly proportional to the system waste strength, but are still one to two orders of magnitude greater than those for synthetic systems.

(2) For lime-treated primary and secondary effluents there appears to be a correlation between pK_{CaCO_3}- and pH values.

TABLE 1

Experimental pK_{CaCO_3}-values for Various Lime-Treated Effluents (MERRILL and JORDEN, 1974)

Effluent type	pK_{CaCO_3}
Well Water	7,4
Primary and secondary effluent	6,7
Raw waste	6,4
Anaerobic digester supernatant	6,3

$Mg(OH)_2$ SOLUBILITY PRODUCT

The magnesium hydroxide thermodynamic solubility product is defined as:

$$K_{Mg(OH)_2} = (Mg^{2+})(OH^-)^2 \quad (4)$$

$$= [Mg^{2+}] \cdot f_{Mg^{2+}} \cdot [OH^-]^2 \cdot f^2_{OH^-} \quad (5)$$

The most recent estimate of this solubility product at 25 °C is:

$$K_{Mg(OH)_2} = 1{,}38 \times 10^{-11} \text{ mol}^3 \ell^{-3} \quad (pK_{Mg(OH)_2} = 10{,}86 \pm 0{,}03)$$

(LIU and NANCOLLAS, 1973). TRUESDELL and JONES (1973) predicted the temperature dependence of this solubility product from thermodynamic considerations, i.e.

$$pK_{Mg(OH)_2} = 10{,}580 + 186{,}15/T \quad (6)$$

Some parameters other than temperature, may affect the magnesium hydroxide solubility product (see calcium carbonate solubility product). MERRILL and JORDEN (1974) calculated magnesium hydroxide solubility product values for lime-treated raw sewage. Unfortunately, no $pK_{Mg(OH)_2}$-values were reported, although a graph was given which showed that the residual dissolved magnesium concentration was a function of pH.

METHODS

Solubility products may be determined either by dissolution or by pre-

cipitation techniques. An objective of this investigation was to establish what constitutes a stable water after precipitation, consequently the precipitation technique was used.

Experimental data was collected from the 4,5 Mℓ d^{-1} Stander Water Reclamation Plant (Pretoria, R.S.A.). In the plant:

(1) lime addition was varied to effect lime reactor effluent pH-values of between 10,5 and 11,5; and

(2) carbon dioxide addition was varied to effect recarbonation reactor effluent pH-values of between 9,0 and 10,5.

To prepare stable lime-treated secondary effluent, a sample of lime reactor effluent was sealed in an airtight glass container and mechanically shaken for 24 hours to attain 'equilibrium'*. Stable recarbonated effluent was prepared in a similar manner, the effluent in this case being withdrawn from the recarbonation reactor. After the 24 hours of mechanical agitation, the suspended solids in a sample were removed by filtration (Whatman No. 542). Immediately after filtration, temperature, pH and total alkalinity of a portion of the filtrate were determined. The remaining portion of the filtrate was acidified to pH 4 with 0,1 N H_2SO_4, to prevent ammonia loss at high sample pH, and analyzed for total dissolved Ca, Mg, NH_3-N, PO_4-P, COD, Na, K, Cl and SO_4.

Using the values for total dissolved Ca, Mg, NH_3-N, PO_4-P, Na, K, Cl, SO_4 as well as pH, total alkalinity and temperature, the ionic strength, free ion concentrations and activities of Ca^{2+}, CO_3^{2-}, Mg^{2+} and OH^- were calculated using computer program WATEQ 1. (This programme is an updated version of WATEQ, published by TRUESDELL and JONES (1973), and includes ion-pairing effects of all the inorganic species analyzed for in the water). Using Eqs. (2 and 5) the K_{CaCO_3}- and $K_{Mg(OH)_2}$-values were calculated.

Once the K-values were available, the influence of the parameters such as pH, temperature and COD on these values could be determined by hypothesizing a basic relationship between the K-value and a specific parameter. The model was then tested by means of computer programme NLIN (MIDDLETON, 1968). The programme estimated model coefficient-values by non-linear least squares regression analysis. For example, the standard relationship for modelling the effect of temperature on equilibrium constants is (TRUESDELL and JONES, 1973):

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* All solubility product values reported in this paper can be regarded as psuedo values since an infinite period of time is required for the attainment of true equilibrium.

$$pK = A + B \cdot T + C/T \quad (7)$$

Using paired sets of values of pK and T as input data, the programme calculated the values of A, B and C to give the best fit to pK- and T-values. The statistical significance of the calculated fit to experimental data is given by the standard error (S.E.), i.e.

$$S.E. = \left(\frac{\text{sum of the squares of residuals}}{\text{degrees of freedom}}\right)^{\frac{1}{2}} \quad (8)$$

$$= \left[\frac{\Sigma(Obs.-Pred.)}{(N - K)}\right] \quad (9)$$

where: Obs. is observed value; Pred. is predicted value; N is the number of observed values; and K is the number of model coefficient values. The fluctuation of observed values about predicted values is indicated by the percentage scatter (P.S.), i.e.

$$P.S. = \left(\frac{\Sigma[(Obs. - Pred.)/Pred.)]}{(N - K)}\right)^{\frac{1}{2}} \times 100 \quad (10)$$

When comparing two models for the same data, the criterion for significant improvement in the calculated fit, was taken as a decrease of at least ten per cent in the standard error.

RESULTS AND DISCUSSION

The chemical quality of (1) secondary- (2) stable lime-treated - and (3) stable recarbonated effluents investigated, is indicated by the ranges of their chemical constitutents listed in Table 2. The quality of the secondary effluent was relatively stable except for ammonia-nitrogen concentration fluctuations. The treated effluents showed marked quality response to different treatment conditions, illustrated by their wide concentration ranges for total alkalinity, calcium, magnesium and pH.

TABLE 2

Quality Ranges of Secondary-, Stable Lime-Treated- and Stable Recarbonated Effluents

Parameter	Secondary effluent		Stable lime-treated effluent		Stable recarbonated effluent	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Temperature (°C)	14,5	20,3	8,0	22,5	17,0	29,5
pH	7,40	7,84	9,64	11,55	8,20	10,85
Total alkalinity (mg ℓ^{-1} as $CaCO_3$)	95	138	75	167	36	136
Calcium (mg ℓ^{-1} as Ca)	36	44	40	86	20	55
Magnesium (mg ℓ^{-1} as Mg)	14	19	<1	18	-	-
Ortho-phosphate (mg ℓ^{-1} as P)	4,2	9,6	<0,2	2,5	-	-
COD (mg ℓ^{-1} as O)	20	42	12	30	-	-
NH_3-N (mg ℓ^{-1} as N)	0,7	8,8	0,8	6,1	1,2	5,8

$CaCO_3$ SOLUBILITY PRODUCT FOR STABLE LIME-TREATED EFFLUENT

Calcium carbonate solubility product values, K'_{CaCO_3}, were calculated [Eq. (2)] for stable lime-treated effluent. Fitting Eq. (7) to 70 data points gave:

$$pK'_{CaCO_3} = 25,237 - 0,0291 \cdot T - 2910,22/T \qquad (11)$$

Correlation between experimental data and the fitted curve is shown in Fig. 1. The standard error was 0,077 which was well within the experimental error of $\pm$ 0,16. Data scatter of 1,12 per cent was obtained about the fitted curve.

The predicted effect of temperature on pK'_{CaCO_3} gave an increase of 0,05 for an increase of ten degrees Celsius, which was of the same order of magnitude as for the synthetic system, i.e. 0,08. The K'_{CaCO_3}-values for the stable lime-treated effluents were approximately one and a half orders of magnitude smaller than those for the synthetic system, at any given temperature (Fig. 2). This significant difference could not be correlated to any one of the major parameters characterizing either the secondary effluent, i.e. COD, NH_3-N, PO_4-P and Mg, or the parameters characterizing the stable lime-treated effluent, i.e. pH, COD, NH_3-N and Mg. The reduction in magnitude of pK_{CaCO_3} could be attributed only to the overall heterogeneity of the secondary effluent. Within the limits of this study, the degree of lime treatment had no significant effect on the resulting equilibrium activity product of calcium and carbonate ions.

Since an estimate of the calcium carbonate solubility product was now available [Eq. (11)], values for calcium carbonate supersaturation could be calculated. The degree of supersaturation (D.S.) in a synthetic system is defined as:

$$D.S. = \frac{(Ca^{2+})(CO_3^{2-})}{K_{CaCO_3}} \qquad (12)$$

and is modified as follows for stable lime-treated effluent:

$$D.S.' = \frac{(Ca^{2+})(CO_3^{2-})}{K'_{CaCO_3}} \qquad (13)$$

A water is at equilibrium with respect to $CaCO_3$ when the degree of supersaturation is unity.

A few typical degree of supersaturation values for lime reactor and primary clarifier effluents were calculated [Eqs. (12 and 13)] and are presented in Table 3. When Eq. (12) was used, as is the normal practice (since K_{CaCO_3}-values for heterogeneous systems were not known), both these effluents appeared considerably oversaturated, i.e. they had high D.S. values. However, when using Eq. (13) the effluents appeared close to

saturation, i.e. D.S. values were approximately unity. The lime reactor effluent was further stabilized by passage through the primary clarifier (Table 3).

$CaCO_3$ SOLUBILITY PRODUCT FOR STABLE RECARBONATED EFFLUENT

Calcium carbonate solubility product values, K''_{CaCO_3}, were calculated [Eq. (2)] for stable recarbonated effluent. The standard form of the equilibrium constant-temperature relationship [Eq. (7)] was fitted to the calculated solubility product values using computer programme NLIN. The standard error in fitted pK''_{CaCO_3}-values was 0,313, indicating that another factor was probably influencing the pK''_{CaCO_3}-values, and different parameters were considered. Correlating pK''_{CaCO_3} with pH- and T values according to:

$$pK''_{CaCO_3} = A + B \cdot T + C/T + D \cdot pH \qquad (14)$$

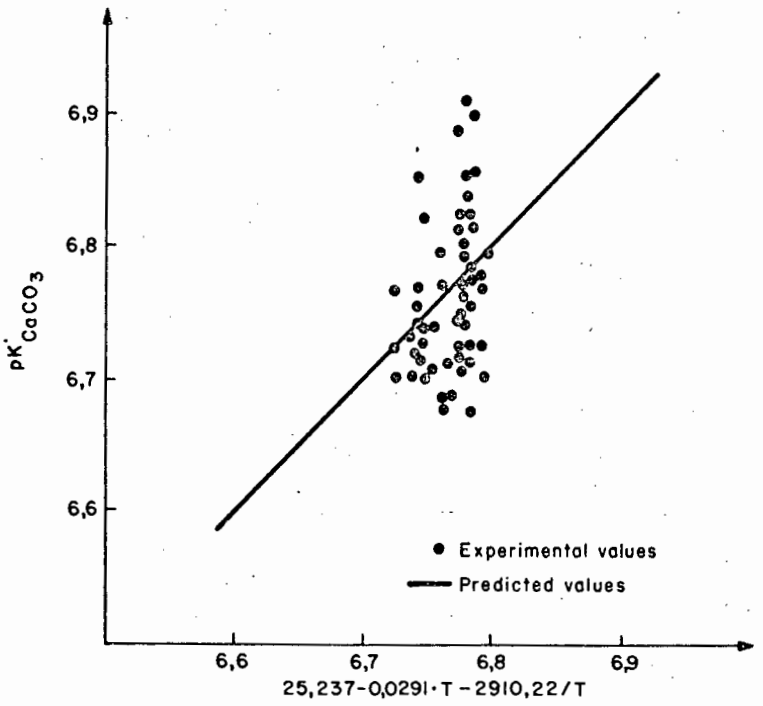

FIG. 1 Calcium Carbonate Solubility Product Values for Stable-Lime Treated Effluent.

resulted in a significantly improved (54% in S.E.) fit of predicted to experimental values, indicating that there was a significant correlation. The coefficient values: A = 24,526, B = -0,0255, C = -1635,66 and D = -0,502, were obtained from a fit to 60 data points. The standard error in fitted pK''_{CaCO_3}-values was 0,144, which was of the same order of magnitude as the experimental error of $\pm$ 0,10. Data scatter was 1,90 per cent about the fitted pK''_{CaCO_3}-values. The correlation between experimental and predicted pK''_{CaCO_3}-values [Eq. (14)] is shown in Fig. 3.

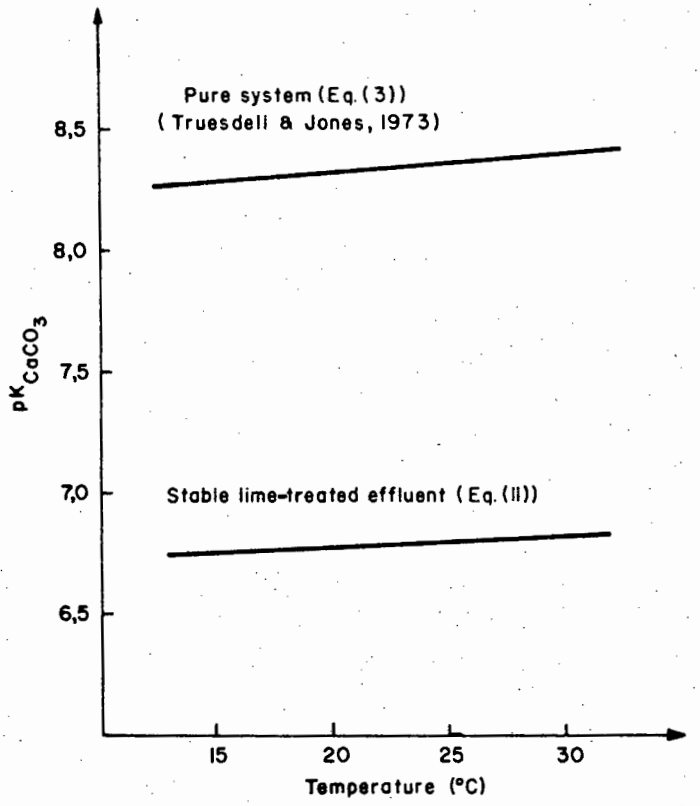

FIG. 2 Predicted Calcium Carbonate Solubility Product Values.

TABLE 3

Typical Values for $CaCO_3$ Degree of Supersaturation for Lime Reactor and Primary Clarifier Effluents

Lime reactor effluent			
pH	Temperature	Degree of supersaturation	
-	°C	Synthetic system*	Real life system**
11,32	22,1	78,94	2,18
10,90	22,5	52,91	1,46
10,72	19,9	52,44	1,48
11,05	19,4	66,28	1,87
11,26	19,2	89,65	2,54
Primary clarifier effluent			
11,10	17,5	48,58	1,39
10,89	20,8	48,02	1,34
11,20	17,0	34,94	1,00
11,49	17,0	46,15	1,33
10,57	16,0	48,92	1,41

* Calculated using the thermodynamic K_{CaCO_3}-value

** Calculated using the predicted K'_{CaCO_3}-value

Calcium carbonate solubility product values for a synthetic system [Eq. (3)] and stable recarbonated effluent [Eq. (14)] were plotted as functions of temperature at different pH-values (Fig. 4). Again the experimentally-derived pK-values were approximately one to one and a half orders of magnitude smaller than the thermodynamic pK-values. The modelled effect of temperature on pK''_{CaCO_3} was a 0,033 decrease for an increase of ten degrees Celsius, as compared with a 0,082 increase for the synthetic system. This discrepancy was not significant when compared with the overall effect of the heterogeneity of the stable recarbonated effluent, particularly the pH. The effect of pH on pK''_{CaCO_3} was significant, i.e. a 0,251 decrease for a 0,5 increase in pH. The pK-values for calcium carbonate in synthetic systems are pH dependent only if the $CaCO_3^o$ ion-pair concentration is considered significant (LANGMUIR, 1968). Experimental pK''_{CaCO_3}-values were recalculated excluding the $CaCO_3^o$ ion-pair from the calculations. The solubility product values remained pH dependent, demonstrating that the pH effect for stable recarbonated effluent existed independent of $CaCO_3^o$ ion-pair considerations.

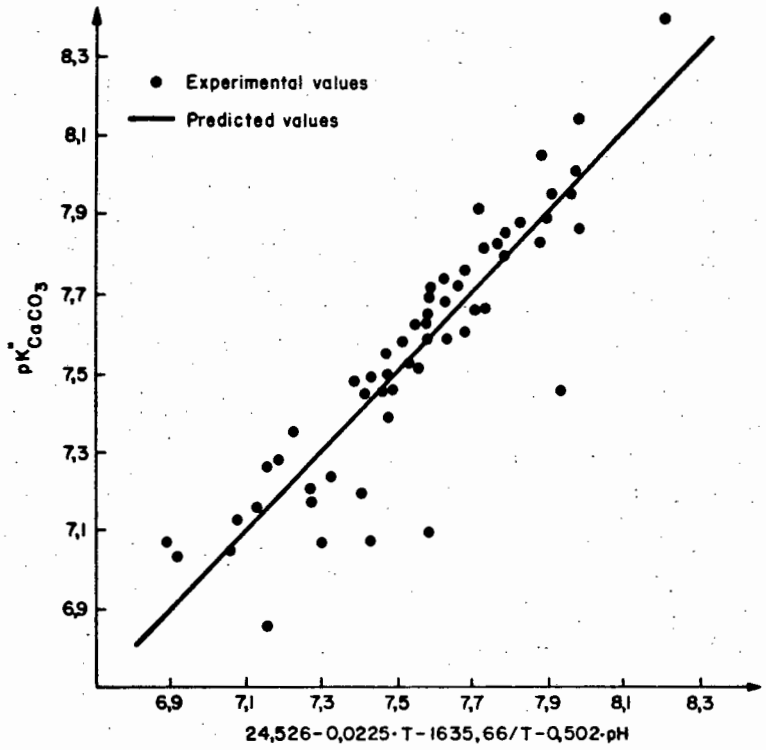

FIG. 3 Calcium Carbonate Solubility Product Values for Stable Recarbonated Effluent.

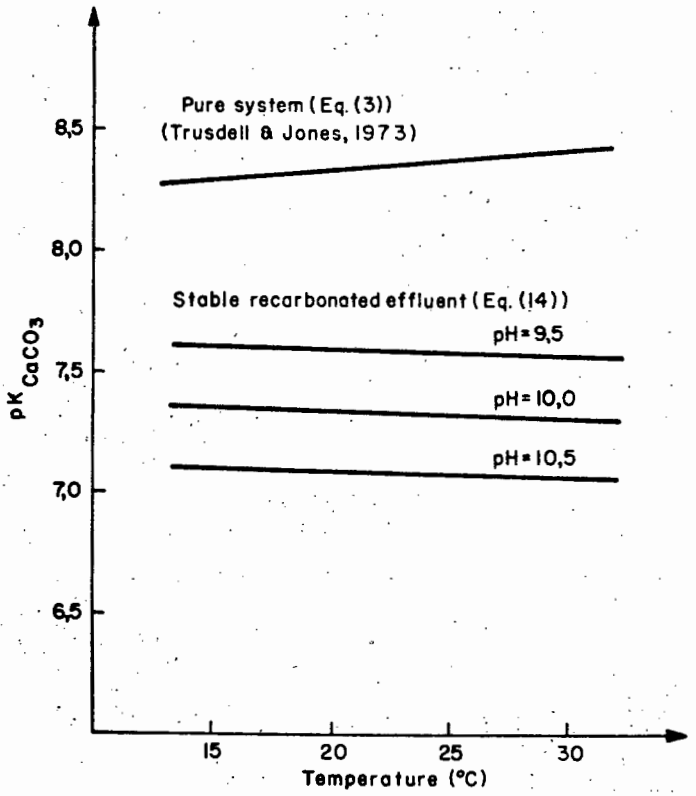

FIG. 4 Predicted Calcium Carbonate Solubility Product Values.

Calcium carbonate solubility product values for synthetic systems, stable recarbonated effluent and stable lime-treated effluent become progressively larger with increasing waste strength. MERRILL and JORDAN (1974) made similar observations and found pK_{CaCO_3}-values for lime-treated well water to be closest to those for the synthetic system, whereas lime-treated anaerobic digester effluent had the lowest reported pK_{CaCO_3}-values (Table 1). Their pK-values for lime-treated raw sewage were of the same order of magnitude as those found in this investigation for stable lime-treated secondary effluent.

Several reasons have been proposed to explain the increased calcium carbonate solubility in heterogeneous systems. LARSON et al. (1973) and DONER and PRATT (1969) attributed this phenomenon to the formation of ion-pair complexes of calcium with bicarbonate, hydroxide and sulphate ions, i.e. $CaHCO_3^+$, $CaCO_3^o$, $CaOH^+$ and $CaSO_4^o$. These ion-pair complexes have, however, been taken into consideration in the calculation of free Ca^{2+} and CO_3^{2-} concentrations in this paper, thus eliminating or reducing the probability of this hypothesis completely explaining the phenomenon of increased solubility. The possibility of free calcium complexing with dissolved organic matter was considered, but could, at best, only account for one fifth or

less of the supersaturated calcium carbonate in solution. REDDY and NANCOLLAS (1973) reported on the severe inhibition of calcium carbonate crystallization by very low concentrations of phosphates. This inhibition was attributed to phosphate adsorption on crystal growth sites. The increased calcium carbonate solubility may thus be attributed to the blocking of crystal growth sites by phosphates, and for that matter, magnesium and organic compounds, which are present in heterogeneous waters.

$Mg(OH)_2$ SOLUBILITY PRODUCT FOR STABLE LIME-TREATED EFFLUENT

Magnesium hydroxide solubility product values, $K'_{Mg(OH)_2}$, were calculated [Eq. (5)] for stable lime-treated secondary effluent. The standard equilibrium constant-temperature relationship [Eq. (7)] was fitted to the calculated solubility product values using NLIN. The standard error in fitted $pK'_{Mg(OH)_2}$-values was 0,346. An attempt was made to obtain a better fit by including major parameters characterizing the secondary effluent and the stable lime-treated effluent in Eq. (7). Of these, only the pH of the stable lime-treated effluent could be correlated with $pK'_{Mg(OH)_2}$-values to give

$$pK'_{Mg(OH)_2} = -82,464 + 0,162 \cdot T + 17988,7/T - 1,443 \cdot pH \qquad (15)$$

The above relationship was obtained from a fit to 28 data points (only data sets with Mg >2 mg ℓ^{-1} and pH >10,5 were used). The standard error in fitted $pK'_{Mg(OH)_2}$-values was 0,207, which was of the same order of magnitude as the experimental error of $\pm$ 0,21. A data scatter of 2,05 per cent about the fitted pK-values was obtained (Fig. 5).

Magnesium hydroxide solubility product values for synthetic systems and stable lime-treated effluent as a function of temperature, are illustrated in Fig. 6. The pK'-values were, again, lower for the synthetic system by approximately zero to two orders of magnitude. The modelled effect of temperature on $pK'_{Mg(OH)_2}$-values showed a decrease of 0,488 for an increase of ten degrees Celsius. However, from thermodynamic considerations TRUESDELL and JONES (1973) predicted a value of only 0,022. LOEWENTHAL and MARAIS (1973), after reviewing the literature on $pK_{Mg(OH)_2}$-values, in which significantly different values were reported, concluded that the $pK_{Mg(OH)_2}$-temperature dependence for synthetic systems may be as follows: an increase of 0,175 for an increase of ten degrees Celsius. The difference in the values reported in the literature and those reported here, is attributed to the heterogeneity of the stable lime-treated effluent.

The pH effect on $pK'_{Mg(OH)_2}$-values was significant, i.e. a 0,5 unit increase in pH corresponded to a 0,70 decrease in $pK'_{Mg(OH)_2}$-value. MERRILL and JORDAN (1974) have also reported pH dependence of $pK_{Mg(OH)_2}$-values for lime-treated raw sewage. It was at first thought that the $MgOH^+$ ion-pair incorporated in the equilibrium species calculation sequence

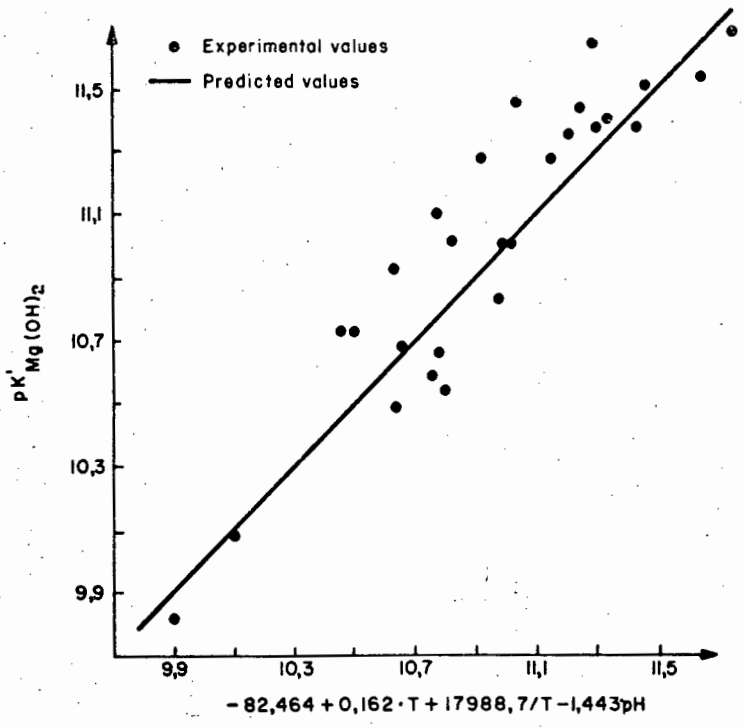

FIG. 5 Magnesium Hydroxide Solubility Product Values for Stable Lime-treated Effluents

may have been responsible for this effect. However, recalculation of $pK'_{Mg(OH)_2}$-values excluding the $MgOH^+$ ion-pair, did not result in a lowering of the pH-$pK'_{Mg(OH)_2}$ correlation. The effect of pH may be attributed to the two forms of $Mg(OH)_2$ proposed by GJALDBAEK (1925). He suggested a labile form obtained by precipitation of magnesium salts by a base, which was reported to have a high solubility. This corresponded to low $pK'_{Mg(OH)_2}$-values at high pH-values. A stable form resulting from recrystallization from the labile form was also reported, with a somewhat lower solubility. It is probable that the stable form will precipitate at lower degrees of supersaturation (i.e. lower pH-values). This would correspond to high $pK'_{Mg(OH)_2}$-values at low pH-values.

Values for magnesium hydroxide degree of supersaturation of lime-treated effluents can now be calculated using $K'_{Mg(OH)_2}$-values. Typical values for the Stander Water Reclamation Plant lime reactor and primary clarifier effluents are given in Table 4. For primary clarifier effluent the degree of supersaturation was less than unity in most cases, indicating that the effluent was slightly undersaturated with respect to magnesium hydroxide. This undersaturation may have been due to the addition of an acidic ferric chloride solution, which was added to lime reactor effluent to flocculate suspended precipitates. The predicted results are therefore not unreasonable.

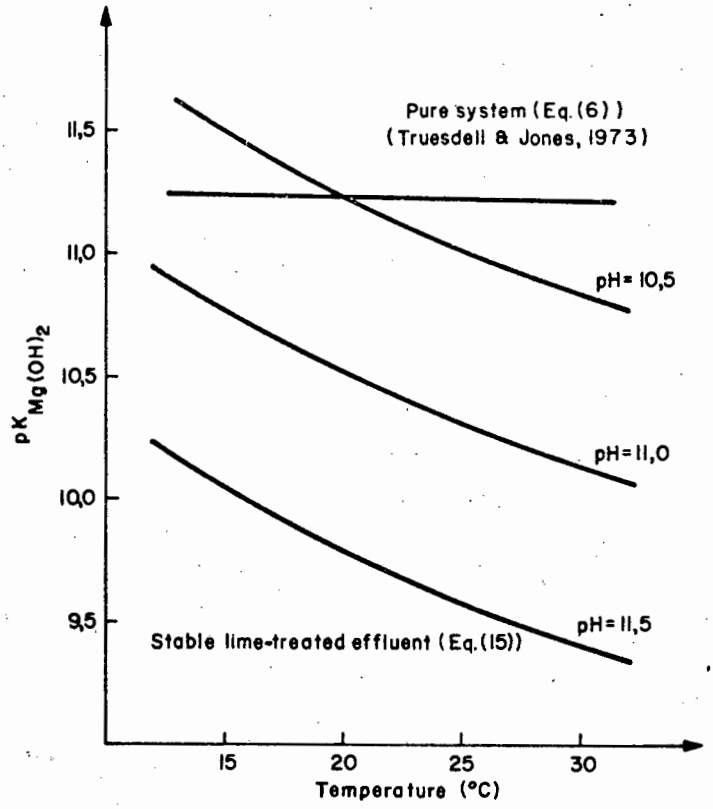

FIG. 6 Predicted Magnesium Hydroxide Solubility Product Values.

TABLE 4

Typical Values for $Mg(OH)_2$ Degree of Supersaturation for Lime Reactor and Primary Clarifier Effluents

pH	Temperature	Degree of supersaturation	
		Lime reactor effluent	
	°C	Synthetic system*	Real life system**
11,32	22,1	19,85	1,11
10,90	22,5	10,40	2,26
11,05	20,2	50,05	2,10
11,40	21,1	9,41	0,44
10,67	20,5	3,49	2,00
		Primary clarifier effluent	
11,10	17,5	4,10	0,77
10,89	20,8	2,67	0,71
11,20	17,0	2,21	0,32
11,49	17,0	7,18	0,39
10,57	16,0	1,25	1,60

* Calculated using the thermodynamic $K_{Mg(OH)_2}$-value

** Calculated using the predicted $K''_{Mg(OH)_2}$-value

CONCLUSIONS

Calcium carbonate and magnesium hydroxide solubility product values were determined for lime-treated secondary effluent. Empirical models correlating these solubility product values with major parameters characterizing the stable lime-treated effluent were established, i.e.

$$pK'_{CaCO_3} = 25,237 - 0,0291 \cdot T - 2910,22/T \quad (16)$$

$$pK'_{Mg(OH)_2} = -82,464 + 0,162 \cdot T + 17988,7/T - 1,443 \cdot pH \quad (17)$$

K'_{CaCO_3} was a function of temperature only. Compared with K_{CaCO_3} for synthetic systems, K'_{CaCO_3} was larger by one and a half orders of magnitude. $K'_{Mg(OH)_2}$ was a function of both temperature and pH. This pH dependence appeared to be related to the two forms of $Mg(OH)_2$, i.e. labile and stable, which precipitated from solution.

Calcium carbonate solubility product values determined for stable recarbonated effluent fitted the following empirical model:

$$K''_{CaCO_3} = 24,526 - 0,0225 \cdot T - 1635,66/T - 0,502 \cdot pH \quad (18)$$

K''_{CaCO_3} was a function of both the temperature and pH, whereas for synthetic systems K_{CaCO_3} was a function of temperature only. K''_{CaCO_3} was larger than K'_{CaCO_3} by one to one and a half orders of magnitude.

Solubility product values determined in this study closely agreed with those reported in the literature for lime-treated sewage and other heterogeneous effluents. It would therefore appear that, although the K'_{CaCO_3}, K''_{CaCO_3} and $K'_{Mg(OH)_2}$ were determined for treated secondary effluent, their application would not be limited to that effluent only. Consequently, calculations of equilibrium concentrations of calcium and magnesium in most treated sewage effluents can be made. These calculations give values more closely related to values obtained in practice, than calculations based on K_{sp}-values for synthetic systems.

Realistic calculations can be made for calcium carbonate and magnesium hydroxide degree of supersaturation of lime-treated secondary effluent, and calcium carbonate degree of supersaturation of recarbonated effluent. Hence the extent of reaction completion within precipitation reactors, and effluent stability can be estimated.

SYMBOLS

$( )$	=	Activity (mol ℓ^{-1})
$[ ]$	=	Concentration (mol ℓ^{-1})
f_x	=	Activity factor of ion x
K_{sp}	=	Thermodynamic solubility product (general term)
K^x_{sp}	=	Thermodynamic solubility product of substances x
K'_{CaCO_3}	=	$CaCO_3$ solubility product for stable lime-treated secondary effluent (mol^2 ℓ^{-2})
K''_{CaCO_3}	=	$CaCO_3$ solubility product for stable recarbonated effluent (mol^2 ℓ^{-2})
$K'_{Mg(OH)_2}$	=	$Mg(OH)_2$ solubility product for stable lime-treated secondary effluent (mol^3 ℓ^{-3})
pK_x	=	Negative logarithm of K_x
T	=	Absolute temperature (^oK)

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Prof G. v.R. Marais of the University of Cape Town for his interest and encouragement of this work, and valuable advice on the compilation and presentation of this paper. The staff of the NIWR for assistance rendered. The Director of the NIWR for permission to present this paper. This work will be used towards a higher degree at the University of Cape Town.

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Calcium Carbonate and Magnesium Hydroxide Solubility Product Values for Heterogeneous Systems *by* N.S. Wiechers, pp. 531 - 545.

Discussion by J.G. Parker, Australia

Can the equations presented in this paper be used for effluents other than secondary effluent, i.e. high strength sewage. What is the effect of ion pairing. Was there any correlation between pk values, COD and Mg^{2+}. How do these improved k-values affect the well established indices such as the Langelier and Ryzner Stability Indices.

Discussion by W. Stumm, Switzerland

The author has presented interesting results on the extent of oversaturation of calcium carbonate and magnesium hydroxide in lime-treated sewage effluent. I object, however, to the terminology used in this paper. It is highly misleading to speak of solubility products. In the systems investigated the approach to equilibrium is extremely slow because organic matter and phosphate inhibit or retard nucleation and crystal growth of these solids. In order to establish equilibrium solubility products, it would be necessary to approach this equilibrium both from oversaturated solutions and from undersaturated solutions, or one would have to look more closely into the time dependence of the oversaturation.

It would also be desirable in such studies to have information on the solid phases formed. Is brucite or another magnesium hydroxide or carbonate actually being precipitated? Is the calcium carbonate precipitated a pure calcite or is it a magnesium calcite?

The organic matter present does not primarily interact by complex formation with Mg^{2+} or Ca^{2+}.

Because the results given represent kinetic rather than equilibrium information, they have to be applied with caution in the interpretation of the 'stability' of lime-treated and re-carbonated sewage effluent.

Discussion by D.G. Vanselow, Australia

What is the effect of ionic strength on the k-values.

Discussion by Mr. Bristoff, Australia

The use of a computation involving levels of ammonia, phosphate, hydroxide and total alkalinity to calculate levels of carbonate in solution appears to be inappropriate in the complex 'heterogeneous' solutions described by the author. Is there any evidence that only the above substances contribute to total alkalinity? In particular, what is the contribution of dissolved organic matter?

Discussion by Mr. Patell, Australia

It was noted that reactions were allowed to proceed to equilibrium in closed vessels. However, samples were analysed after filtration. Did the alkaline effluent absorb carbon dioxide from the air during filtration.

Calculations of carbonate ion concentrations were based on alkalinity and pH measurements. Was inorganic carbon analysis considered?

Discussion by J. Zoltek, U.S.A.

Was the effect of time on the activity products studied? Was the precipitation of $MgCO_3$ considered? The fit illustrated in Fig. 1 appears poor whereas the standard error for these results is reported as very low.

Degree of supersaturation (DS) as defined by equation [12] in the paper is a quantity which bears little relationship to parameters normally used by engineers. Taking the n-th root of DS will give a more intuitively meaningful quantity which may be related to units of concentration.

Discussion by W. Weber, U.S.A.

Prof. Weber did not completely agree with statements made by Prof. Stumm. He believes that thermodynamic equilibrium will not be established within 24 hours, but the determined activity products may be interpreted as kinetic intermediate values, which in themselves may be of significant practical value. Organic matter may form complexes with calcium and magnesium, although removal by adsorption on to calcite is perhaps more likely.

Replies

The equations presented in this paper were specifically developed for secondary effluent. However, literature values for high strength sewage are indicated in the paper. In addition, the equations presented will give better approximations for true activity products than calculations based on the solubility products of calcite and brucite.

The ion pairing effect is significant for species such as $CaCO_3^o$, i.e. at pH 10,5, 25% or more of the total dissolved calcium may be bound in the form of the $CaCO_3^o$ ion pair.

No detectable correlation between pk values, COD and Mg^{2+} could be measured for this specific effluent, as explained in the paper.

The Langelier and Ryznar Stability Indices are based on the calcite solubility product. A realistic application of these indices to lime treated secondary effluent requires that the calcite solubility product be replaced by the newly developed 24 hour activity products presented in this paper.

The results presented in this paper have been applied to establish if precipitation reactor residence times were sufficiently long enough to give effluents of an acceptable stability.

I agree with Professor Stumm that the term 'solubility product values' was an incorrect designation for these values and I propose to call them '24 hour activity products'. A number of tests were conducted to establish the effect of time periods. Reaction periods of 2,4,6,8,10,15,30,60, 120 minutes, 24,48,100,200 and 250 hours were studied. The tests indicated that the activity products for secondary effluent stabilized after approximately 60 minutes. For this reason a convenient reaction period of 24 hours was chosen and considered as a reasonable reaction period to obtain a stable effluent. However, it is true that the reaction did proceed further, even at 24 hours, and hence thermodynamic equilibrium had not been established.

The purpose of the study, as pointed out in the paper, was to characterise the 'stable' state an effluent would attain after lime treatment and recarbonation. For this reason only precipitation and not dissolution, was considered.

Sludge produced in the precipitation processes was subjected to microscopic, electro micrographic and X-ray analysis. Calcite was positively identified. Brucite was not positively identified. There may be several reasons for this : firstly, the concentration of $Mg(OH)_2$ in the sludge is very low, i.e. 1 - 3%, secondly it is doubtful whether brucite formed

under some of the experimental conditions tested, as indicated in the paper. Magnesium calcite was not identified.

The author agrees that results presented in this paper must be applied with caution in the interpretation of the 'stability' of lime-treated waters. However, the equations presented in this paper will give considerably better approximations than those obtained from calculations based on the solubility of calcite and brucite.

The ionic strength effects were incorporated in calculations through the ion activity factors as indicated by equations [2] and [5] in the paper. The Davies equation was used to calculate activity factors from ionic strength values.

It was found that the lime treated effluent did absorb carbon dioxide from the air. pH measurements were taken before and after filtration, and the value usually dropped by between 0,05 to 0,20 pH units. However, it was essential to filter samples to give accurate alkalinity values. It was therefore attempted to minimize the problem by (a) allowing suspended solids to settle in the reaction flasks and only filtering clear supernatant, (b) taking care to minimize air-water contact by fast vacuum filtration.

Inorganic carbon analysis was considered as a method for measuring carbonic species concentrations. However, the accuracy of inorganic carbon analysis equipment used at the NIWR during the period that this work was done, was poor and unreliable. The alkalinity, pH, temperature, ionic strength and accompanying ion-pairing calculations gave the most reliable carbonate concentration values for this type of system.
Lime treated effluents were considerably more oversaturated with respect to brucite than $MgCO_3$, and hence it was considered more likely that $Mg(OH)_2$ would precipitate than $MgCO_3$. The carbonate ions are also more likely to be precipitated as $CaCO_3$ than $MgCO_3$, due to high calcium concentration relative to magnesium concentrations. It is likely that some magnesium calcite precipitated although the concentration was too low to be detected by X-ray analysis.

The experimental pk_{CaCO_3} values for lime treated effluent were found to be approximately constant, i.e. 6,8 $\pm$ 0,1, whereas for recarbonated values, it varied significantly, i.e. 7,5 $\pm$ 0,6. The pk scale in Fig. 1 is considerably larger than in Fig. 3. What Fig. 1 illustrates is that there is little correlation between variations in pK values (the variations being relatively small) and temperature variations. The variations in pK values appear to be mainly due to random experimental errors.

Carbonate, bicarbonate, hydroxide, ammonia and orthophosphate where the major components contributing to the alkalinity of the effluent which was studied. The level of dissolved organic matter was relatively low, i.e. within the range of 10 to 30 mg ℓ^{-1} as O_2, and hence it is doubtful whether this made any sifnificant contribution to the effluent's alkalinity.

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